

PORTLAND HARBOR RI/FS
REMEDIAL INVESTIGATION REPORT

APPENDIX C2
**GROUNDWATER PATHWAY ASSESSMENT AND
GEOCHEMICAL ANALYSIS**

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June 12, 2015

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LIST OF ACRONYMS

2,4-D	(2,4 dichlorophenoxy) acetic acid
2,4-DB	4-(2,4-dichlorophenoxy)butyric acid/esters
BaP	benzo(a)pyrene
bgs	below ground surface
bml	below mudline
BTEX	benzene, toluene, ethylbenzene, and total xylene
COI	contaminant of interest
CRBG	Columbia River Basalt Group
CVOC	chlorinated volatile organic compound
DCA	dichloroethane
DCB	dichlorobenzene
DCE	dichloroethene
DDT	dichloro-diphenyl-trichloroethane
DEQ	Oregon Department of Environmental Quality
DNAPL	dense nonaqueous-phase liquid
FAMM	Fuel and Marine Marketing Inc.
FSP	field sampling plan
FSR	field sampling report
GWPA	groundwater pathway assessment
HPAH	high-molecular-weight polycyclic aromatic hydrocarbon
IRAM	Interim Remedial Action Measure
JSCS	Joint Source Control Strategy
KI	Koppers Industries
KMLT	Kinder Morgan Linnton Terminal
LNAPL	light nonaqueous-phase liquid
LNG	liquefied natural gas
LPAH	low-molecular-weight polycyclic aromatic hydrocarbon
LWG	Lower Willamette Group
MCB	monochlorobenzene
MCPA	4-chloro-2-methylphenoxyacetic acid
meq/L	milliequivalents per liter
MGP	manufactured gas production
MPR	manufacturing process residue
MSL	mean sea level
MTBE	methyl tert-butyl ether
NAPL	non-aqueous phase liquid
ORP	oxidation-reduction potential
PAH	polycyclic aromatic hydrocarbon
PEO	Premier Edible Oils
PG&C	Portland Gas & Coke
RAO	remedial action objective
RI	remedial investigation
RM	river mile

RPD	relative percent difference
SAP	sampling and analysis plan
SCRA	site characterization and risk assessment
SI	saturation index
SIC	Schnitzer Investment Corporation
SPI	Sediment Profile Imagery
SRM	Sandy River Mudstone
SVE	soil vapor extraction
TCA	trichloroethane
TCE	trichloroethene
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TZW	transition zone water
USEPA	U.S. Environmental Protection Agency
WBZ	water-bearing zone

C1.0 INTRODUCTION

This appendix provides a summary and detailed analysis of data collected in the Groundwater Pathway Assessment (GWPA) for the Portland Harbor Superfund Site (Study Area)¹ Remedial Investigation (RI). The GWPA was performed to provide information to determine whether contaminants of interest² (COIs) associated with known upland groundwater plumes were, at the time the GWPA was conducted, discharging to the Study Area (due to current and/or historical sources), thus creating a complete transport pathway for such COIs to reach the groundwater/surface water transition zone³ in Study Area sediments. The analysis presented in this appendix focuses on the presentation of multiple lines of evidence that support the identification of probable groundwater discharge areas and patterns in transition zone water (TZW) and bulk sediment chemistry within these areas. The data and analysis presented herein provide the basis for the evaluation in the RI Section 4 of groundwater plumes as a potential source of COIs to the Study Area and support the baseline human health and ecological risk assessments, which include evaluations of whether the discharge of these COIs contributes to unacceptable risks to human health and/or the environment. Section 5 of the RI presents the TZW sampling results generated by the LWG during the RI and by individual parties under Oregon Department of Environmental Quality (DEQ) source control investigations.

The contents of this appendix are organized as follows:

- The remainder of this introduction (Section 1) presents background information regarding the conceptual underpinnings of the GWPA, a description of the general hydrogeologic setting of the Study Area, and an overview of the main elements of the GWPA work conducted for the RI.
- Section 2 details the process by which the U.S. Environmental Protection Agency (USEPA), DEQ, and the Lower Willamette Group (LWG) jointly identified nine upland groundwater sites along the shoreline of the Study Area where there exists a confirmed or reasonably likely complete groundwater transport pathway for COIs to migrate to TZW.

¹ The current Study Area boundaries encompass the 9.9-mile stretch of the Willamette River from approximately river mile (RM) 1.9 to 11.8.

² Prior deliverables and some of the tables and figures attached to this document may use the term “chemical of interest,” which has the same meaning as “contaminant of interest” and refers to “contaminants” as defined in 42 USC 9601(33).

³ The groundwater/surface water transition zone (also known as the hyporheic zone) is the interval where sediment pore water consists of a mixture of groundwater and surface water. The transition zone is a complex environment in which physical (e.g., advection and diffusion), chemical (e.g., redox conditions and sorption), and biological (e.g., bioturbation and chemical biotransformation) processes can affect chemical transport, distribution, and fate in bulk sediment and interstitial pore water. The depth of the transition zone depends on sediment texture, groundwater advective flux, and tidal influences in the water column.

- Section 3 presents the findings of the GWPA, focusing on whether groundwater discharges offshore of each of the nine study sites are creating a complete chemical transport pathway for COIs in upland groundwater plumes to reach TZW in the Study Area. This section presents a site-by-site assessment, using multiple lines of evidence to identify probable areas of upland groundwater plume discharge. This section does not attempt to re-present all data generated in the GWPA, relying instead on the nature and extent presentation of the TZW data sets in Section 5.4 of the main RI report.
- Section 4 provides an analysis of the likely geochemical controls affecting the origin, transport, and fate of arsenic, barium, and manganese in TZW; these metals/metalloids were nearly ubiquitously detected in TZW samples collected from locations throughout the Portland Harbor Study Area, raising questions as to whether their occurrence in TZW is a function of natural conditions (i.e., background), the result of chemical releases and transport to the Study Area via the groundwater pathway, or some combination of these factors.

C1.1 CONCEPTUAL BACKGROUND

The conceptual site model (CSM) initially presented in the Programmatic Work Plan (2004) and updated in Section 10 of the RI Report identifies the groundwater transport pathway as one of several potential transport mechanisms for COIs derived from external sources to reach the Study Area. Recognizing the potential importance of this transport pathway, the GWPA was conceived and implemented to meet the following broad goals outlined by Integral et al. (2004):

1. Provide a sufficient understanding of the hydrogeologic framework, groundwater flow systems, and surface/groundwater interactions within the Study Area
2. Identify upland groundwater plumes where it is confirmed or likely that a complete transport pathway exists for groundwater COIs to reach the Study Area
3. Identify data gaps for assessing the potential effects of those groundwater COIs discharging to the river on human and ecological receptors
4. Conduct an investigation designed to address these data gaps.

Several physical, chemical, and biological mechanisms that may influence the potential transport of COIs (derived from either upland groundwater or in-water sources) via the groundwater pathway were identified in the Programmatic Work Plan. These processes, which are portrayed graphically in Figure C1.1-1, include the three broad categories described below.

Category 1 – processes that may influence the transport of COIs in groundwater along the flow path from upland source areas to the groundwater/surface water transition zone and shoreline seep areas:

- Dissolved transport of groundwater COIs from upland sources through normal advection and dispersion, including transport via preferential flow pathways
- Potential facilitated transport of low-solubility, hydrophobic chemicals as a result of cosolvency effects
- Chemical transformation and attenuation processes—including sorption to aquifer materials and sediments, abiotic chemical degradation/transformation, and aerobic and/or anaerobic chemical biodegradation/biotransformation processes—many of which can result in sequestration, stabilization, and/or remediation of certain upland groundwater COIs before reaching the groundwater-surface water interface
- Seepage of light and dense non-aqueous phase liquid (LNAPL and DNAPL) to river sediments
- Surface expressions of contaminated groundwater and NAPL in shoreline seep areas.

Category 2 – processes that influence the potential remobilization of COIs in surface and/or subsurface sediment:

- Desorption of COIs from sediments
- Diffusive flux of COIs from sediment to the sediment-surface water interface
- Advective-dispersive transport of COIs desorbed from sediments due to groundwater flux through the sediment transition zone.

Category 3 – processes that result in cross-media transfer (i.e., loading) of COIs transported via the groundwater pathway to sediment, surface water, and/or biota:

- Sorption of dissolved groundwater COIs to sediment
- Discharge of groundwater COIs to surface water
- Bioaccumulation of groundwater COIs in organisms that are exposed to contaminated media.

It is important to highlight that the presence of COIs in TZW may be attributable to chemical sources other than upland groundwater plumes and presence by itself does not necessarily indicate the existence of a complete transport pathway from an upland groundwater source to the in-water portion of the Site. Thus, the analysis presented in this document relies on multiple lines of evidence to evaluate, to the extent possible based on available data, whether chemicals detected in TZW may reflect chemical transport from upland groundwater sources, influences on TZW chemistry from in-water sources (e.g., desorption of chemicals in bulk sediment), or some combination.

C1.2 STUDY AREA HYDROGEOLOGY

The Study Area is located along the southwestern edge of the Portland Basin. The basin has been filled with alluvial and glacio-fluvial flood deposits, which overlie older rocks, including the Columbia River Basalt Group (CRBG) and older marine sediments. Because the Study Area is located at the edge of the basin, both the older rocks and overlying sediments are present near the surface and play a significant role in defining interactions between groundwater and the river.

The geologic units found in the vicinity of the Study Area are illustrated in Figure 3.1-1 of the RI Report, and include, from youngest to oldest, the following (Beeson et al. 1991; Swanson et al. 1993):

- **Recent Fill** – Fill blankets much of the lowland area next to the river and is predominantly dredged river sediment, including fine sand and silty sand.
- **Fine-grained Pleistocene Flood Deposits and Recent Alluvium** – This unit generally consists of silt, clay, silty sand, and fine-to-medium sand that borders and underlies the present floodplain of the river.
- **Coarse-grained Pleistocene Flood Deposits** – The unit consists of uncemented sand, gravel, and cobbles with boulders in places that fill deep channels incised into the Troutdale Formation and CRBG.
- **Upper Troutdale Formation** – The upper Troutdale Formation in the vicinity of the LWR includes cemented and uncemented alluvial sand, gravel, and cobbles deposited by the ancestral Willamette and Columbia rivers.
- **Lower Troutdale Formation/Sandy River Mudstone** – The Sandy River Mudstone (SRM) is a fine-grained equivalent (over-bank facies) of the lower Troutdale Formation that overlies the CRBG in the center of the basin and at the margins of the basin away from the axis of the Columbia River. The SRM is not considered a significant hydrogeologic unit within the Study Area.
- **Columbia River Basalt Group** – The CRBG consists of a thick sequence of folded and faulted basalt flows. The CRBG is present at the surface or at relatively shallow depths along the west side of the Study Area and may be in direct contact with the river in places. The top of the unit drops off below ground surface (bgs) over a relatively short distance and is 400 or more feet bgs on the east side of the Study Area.

Up to three general groundwater flow systems of interest are recognized along the Study Area: a shallow, an intermediate, and a deep system (see Figure 3.1-2 of the RI Report). At a local level, the divisions between flow systems can be indistinct in places along the Study Area. Additionally, some investigations have identified further flow system refinements or divisions based on the local hydrogeology. However, the general flow systems described below appear to apply for the majority of the Study Area and provide a general model from which variations can be evaluated on a local scale.

- **Shallow Flow System** – The shallow, unconfined, groundwater flow system along the margins of the Study Area consists mostly of fill and alluvial silt and clay deposits and some medium- to coarse-grained channel sand that blankets the lowlands next to the river. The shallow system is recharged by direct precipitation and infiltration, infiltration from the hills on the west side of the Study Area, and exchange with several surface water bodies along the Study Area (e.g., Doane Lake). Groundwater level data in the upland areas indicate that there is a downward gradient toward deeper units from the shallow system. Groundwater levels and fluxes in the shallow system are affected by seasonal river stage changes, as well as by diurnal tidal influences. The presence of low-permeability features, such as silt and clay dikes constructed to retain hydraulically emplaced dredge fill, cutoff walls, and retaining walls, may act to impede groundwater flow locally in the shallow system. The presence of preferential pathways (human-made and natural) in the shallow system can be a significant influence on the discharge of groundwater to the river.
- **Intermediate Flow System** – The intermediate flow system occurs within thicker sequences of fine-grained alluvial sediments that frequently underlie the shallow zone. Groundwater in the intermediate system generally discharges to the Willamette River below the river surface to deeper portions of the river (see RI Figure 3.1-2), with discharge focused at the locations where more permeable strata (typically sand) may intersect the river.
- **Deep Flow System** – The deep flow system occurs within the coarse-grained flood deposits and basalt interflow zones of the CRBG, where the CRBG is present near the surface on the west side of the river. Downstream of about RM 9 on the west side of the river, residual basalt gravels immediately overlying the CRBG have been identified as important hydrogeologic features and potential conduits for groundwater contaminant transport. Groundwater in the deep system discharges to the Willamette River only in deeper portions of the river, with discharges focused at the locations where the gravels and/or basalt interflow zones are near or intersect the river sediments (see RI Figure 3.1-2). The CRBG does not play a role in the deep flow system on the east side of the river because it occurs at substantially greater depth.

Generally, groundwater flow in the uplands bordering the Study Area converges toward the river. In the absence of preferential pathways or active groundwater remedial actions (e.g., groundwater extraction, barrier walls), groundwater flow to the sediments and river will be diffuse along the length of the interface of each flow system with the river. However, spatial variations in permeability of several orders of magnitude can be expected where alluvial processes create lenses and channels of sand within or surrounding finer-grained materials. The result of these permeability contrasts is that groundwater discharge will be heavily influenced by the location and geometry of higher permeability layers (e.g., sands) in relation to the river.

Discharge from the shallow water-table groundwater system tends to be focused at or below the river/shore interface. Low river stages expose zones of focused discharge as seeps along the bank where the shallow groundwater surface intersects the ground surface. Preferential pathways, including coarse backfill (e.g., around utilities), historic stream channels, or sand/gravel layers can focus groundwater flow, particularly where they occur in predominantly fine-grained sediment sequences in the shallow groundwater system. Groundwater discharge through the river sediments to surface water is controlled by 1) the permeability contrast between the sediments and underlying aquifer, and 2) the difference between the hydraulic head in groundwater at the aquifer/sediment interface and the river stage, which determines the hydraulic gradient.

C1.3 OVERVIEW OF THE GROUNDWATER PATHWAY ASSESSMENT PROCESS

The GWPA consisted of several activities that were designed to identify appropriate technical methods and procedures for conducting in-water groundwater characterization work, identify locations where COIs in groundwater from upland sites may be discharging to the river, and collect samples of TZW to support an assessment of whether any such discharges may pose or contribute to unacceptable risks to in-water receptors. Objectives, procedures, detailed sampling plans, and results for the GWPA field program were summarized in the following documents:

- GWPA Pilot Study Field Sampling Plan (Integral 2004)
- Round 2 GWPA Sampling and Analysis Plan (SAP; Integral et al. 2005)
- SAP Appendix B, GWPA Pilot Study Data Report (Integral 2005d)
- SAP Attachment 1, Groundwater Plume Discharge Mapping Field Sampling Plan (Discharge Mapping FSP; Integral 2005c)
- SAP Attachment 2, TZW FSP (TZW FSP; Integral 2006d)
- TZW FSP Addendum 1 (Integral 2006a)
- TZW FSP Addendum 2 (Integral 2006b)
- Round 2 Quality Assurance Project Plan supplement (Integral 2006c)
- Round 2 GWPA Health and Safety Plan (Integral 2005b)
- Round 2 GWPA Transition Zone Water Site Characterization Summary Report (Integral 2006f).

The main elements of the GWPA are briefly discussed below.

C1.3.1 Groundwater Pathway Assessment Pilot Study

From late 2004 to early 2005, the LWG performed a pilot study that was designed to evaluate groundwater discharge mapping tools and TZW sampling methods for possible use in the GWPA. The technical approach and scope of work for the pilot study was

presented in the GWPA Pilot Study Field Sampling Plan (Integral 2004). Pilot study results were presented in Appendix B of the SAP (Integral 2005d). The pilot study results, in conjunction with guidance available from technical literature sources, formed the basis for the identification of methods presented in the Discharge Mapping FSP (Integral 2005c) and TZW FSP (Integral 2006d).

C1.3.2 Site Selection

During the planning phase of the GWPA, 113 upland sites located between river mile (RM) 2 and 11 were identified and categorized according to potential to represent a source of COIs to Portland Harbor via the groundwater transport pathway (GSI 2003b). Of these, 21 sites were initially identified as “Category A,” defined as those sites with a confirmed or reasonable likelihood for discharge of upland groundwater COIs to Portland Harbor. From this list, USEPA, DEQ, and LWG identified the 12 high-priority Category A sites, shown on Figure C1.3-1. Of these, nine sites were ultimately selected for inclusion in the GWPA. Section C2 of this appendix provides a detailed summary of this selection process.

C1.3.3 Compilation and Review of Updated Site-Specific Background Information for Selected Sites

Detailed background information on site history, chemical sources and releases, stratigraphy, groundwater flow conditions (including potential preferential flow pathways), seeps, and the nature and extent of COIs in groundwater were presented in Appendix A of the SAP and in Addenda 1 and 2 of the TZW FSP (Integral et al. 2005, Integral 2006a, 2006b). This information was considered in the GWPA for each site, and key information is summarized in this appendix.

C1.3.4 Groundwater Discharge Mapping

The groundwater discharge mapping program was completed from August 1 to September 9, 2005. Detailed results of the discharge mapping component of the GWPA are presented in Addenda 1 and 2 of the TZW FSP (Integral 2006a, 2006b) and are not reproduced in this report. The discharge mapping activities focused on suspected areas of groundwater discharge identified based on site summary information. The discharge mapping approach for the GWPA relied on multiple lines of evidence to provide information on the stratigraphic, hydrologic, chemical, and physical conditions that may be indicative of groundwater discharges. This information, in turn, was used to identify appropriate sampling locations for the TZW sampling component of the GWPA. The groundwater discharge mapping field program at each study site consisted of the following elements:

- Offshore stratigraphic borings in select locations to refine the understanding of subsurface stratigraphy in potential groundwater plume discharge areas in the channel of the Willamette River

- Transect-based measurements of shallow transition zone water temperature and conductivity, which can be indicators of differential groundwater discharge conditions
- Qualitative, transect-based mapping of surface sediment texture
- Collection of preliminary field-screening TZW samples in select locations for semi-quantitative identification of distinct chemical indicators of groundwater plume discharge (where applicable)
- Physical verification of groundwater discharges in nearshore areas using seepage meters.

Complete results of the discharge mapping program are presented in Addenda 1 and 2 of the TZW Sampling FSP (Integral 2006a, 2006b). Discharge mapping results for each of the nine study sites are also summarized in this report as part of the integrated evaluation of the groundwater transport pathway and TZW sampling results at each site.

C1.3.5 TZW Sampling

TZW sampling activities were performed as part of Round 2 of the RI between October 3 and December 2, 2005. Samples were collected in the fall because this is typically a period of low river stage and correspondingly higher groundwater hydraulic gradient toward the river. Thus, the sampling period was chosen to obtain TZW samples that would reflect a period of relatively higher groundwater discharge to the river. Sampling locations were selected at each of the nine study sites based on the results of the groundwater discharge mapping field effort.

The findings of the discharge mapping effort were considered in conjunction with relevant site data (e.g., hydrogeology, surface sediment texture delineation, distribution of COIs in upland groundwater and sediments) to identify any zones of possible groundwater discharge. The TZW sampling locations selected for each site focused primarily on the zones of possible groundwater plume discharge, based on the GWPA discharge mapping effort.⁴ Additional sampling locations were specified to provide comparative data for TZW quality outside of the potential discharge zones.

Two sampling tools—the Trident Probe and small volume peepers—were used to collect TZW samples during the Round 2 GWPA. The Trident Probe is a direct-push system equipped with temperature, conductivity, and water sampling probes. TZW is collected through a small-diameter, Teflon[®]-coated, stainless-steel probe equipped with a sample port covered by a small mesh (241- μ m), stainless steel screen. The Trident Probe is driven to the desired depth in the sediment, and water is drawn through tubing connected to the sampling probe using a peristaltic pump. A sand pack is often placed over the sampling probe to prevent/delay clogging of the intake by silt and clay. The Trident

⁴ It should be noted that groundwater discharge zones previously identified were re-evaluated for this report based on all the lines of evidence currently available. Thus, in this report some discharge zones were refined or otherwise updated as a part of the data analysis here.

Probe, which is an effective and efficient tool for sampling transition zone water from coarse-grained sediments, was selected as the primary tool for transition zone water sampling during the Round 2 Groundwater Pathway Assessment. Small volume peepers, which are effective for sampling transition zone water in fine-grained sediments, were employed for sampling from fine-grained sediments, where use of the Trident is impractical. The small-volume peepers used in this investigation were commercially available, plate peepers equipped with 28 rows of sample ports ranging in volume between 3.5 mL and 9 mL. Each peeper is capable of collecting approximately 250 mL of water over a 38-cm sediment depth. Prior to deployment, the small-volume peepers were filled with anoxic deionized (DI) water and fitted with a 5- μ m Teflon membrane to separate the sample ports from the sediments. The entire peeper assembly was maintained in an anoxic (argon-sparged) water bath until immediately prior to deployment. The small-volume peepers were deployed by a diver, who drove or pushed the peepers directly into the sediments until the uppermost sampling port was just below the sediment mudline (i.e., the ports were spaced from 0 to 38 cm below the sediment surface). Multiple peepers were deployed at each sampling location, as necessary, to achieve sufficient sample volume by compositing. All of the peepers were left in place to equilibrate for a period of several weeks, after which they were retrieved and brought to the surface. Water was then extracted from each of the sample ports by inserting a needle through the membrane and extracting the water with a syringe. Each sample bottle was filled with water from sample ports distributed across the entire peeper to ensure that the sample was a vertical composite representative of the entire 38-cm depth of sediment.

Per direction from USEPA (2005c, pers. comm.), unfiltered samples were collected at all Trident Probe sampling locations. Where sufficient pore water volume could be collected prior to clogging of the Trident sampler, filtered samples were also collected. Peeper samples are classified in the SCRA as unfiltered samples because the 5- μ m membrane mesh size is much larger than the standard 0.45- μ m mesh size for filtered samples; however, due to the passive nature of this sampling method, the TZW samples collected using peepers are not expected to be significantly biased by turbidity/particulates. The number of sampling locations with no filtered result varies by analyte and by study site. A discussion of the differences between filtered and unfiltered results is presented in Section C3.0.3 of this appendix.

A total of 155 shallow TZW samples (62 unfiltered Trident, 57 filtered Trident, and 36 peeper samples) were collected during Round 2 at depths of 0–38 cm below the sediment-water interface. An additional 34 TZW samples (23 unfiltered Trident and 11 filtered Trident) were collected during Round 2 from depths ranging from 90 to 150 cm below the sediment-water interface. Bulk sediment samples were collected at a subset (n=34) of the TZW sampling locations, where sediment chemistry data were not available from previous RI/FS sediment sampling for a similar sediment type located within approximately 50 to 100 ft of the TZW sampling location. Key data from these sampling efforts with respect to the GWPA are discussed for each of the nine sites in Section 3 of this appendix. Section 5.4 of the main RI report provides an overall presentation of the results of the TZW sampling. The complete RI data set for TZW for

all sampled chemicals is presented in the project SCRA database (Appendix A) and summarized in Appendix D4, Tables D4-1 and D4-2.

C1.3.6 Round 3 Stratigraphic Coring (Gunderson Area 1 Site)

Based on data gaps identified for the Gunderson Area 1 site after the completion of the Round 2 GWPA investigation, a Round 3 GWPA field investigation was completed at this site from October 16 to 19, 2007. This investigation consisted of collecting nine stratigraphic cores offshore of the Gunderson Area 1 site in accordance with the Round 3 GWPA FSP (Integral 2007b).

C1.3.7 Party-Led Supplemental TZW Investigations

In addition to the GWPA activities summarized above, the upland parties for specific sites have conducted independent in-water investigations since the 2005 site selection analysis (Integral et al. 2005) that supplement the understanding of the groundwater transport pathway to the LWR offshore of these sites. These investigations include the following:

- **Gasco** – NW Natural completed a detailed investigation of the groundwater pathway at the Gasco site in 2007–2008. The investigation included, but was not limited to, stratigraphic coring, characterization of nearshore groundwater, TZW and sediment sampling, and measurement of groundwater seepage rates. Results of this investigation are summarized in Anchor (2008).
- **Siltronic** – Siltronic completed an investigation of nearshore groundwater and TZW quality in 2004–2005. The investigation included, but was not limited to, collection of groundwater and TZW samples and measurement of vertical gradients offshore of the site. Results of this investigation are summarized in MFA (2005).
- **Arkema** – The Final Remedial Investigation Report for the Arkema site was completed in December 2005 (ERM 2005b). A two-phase DNAPL investigation was performed in 2005 and 2006 to delineate chlorobenzene DNAPL in the Acid Plant Area (ERM 2006a), including identification of its shoreward extent. In addition, a partial round of groundwater sampling for select analytes was performed in 2006 (ERM 2006b), and a more comprehensive round of groundwater sampling was performed in 2007 (ERM 2007).
- **Evrax Oregon Steel Mills (EOSM)** – In 2005, EOSM completed an independent assessment of the groundwater pathway involving the installation of shoreline “beach” wells and a geochemical evaluation of the occurrence of specific metals in the transition zone. Results of these investigations are summarized in Retec (2006).
- **Time Oil Northwest Terminal** – Time Oil installed monitoring wells along the shoreline area of the site (beach wells) in 2004 (Brooks 2005, pers. comm.). These beach wells are located downgradient of those along the riverbank and,

therefore provide a more accurate estimate of the potential for a complete transport pathway for groundwater COIs to reach in-river exposure points.

- **Schnitzer Investment Corporation (Premier Edible Oils Site)** – Schnitzer Investment Corporation (SIC) completed an investigation in January/February 2008 to provide supplemental data for the Premier Edible Oils (PEO) site (Gradient and URS 2006). Among other objectives, this investigation was designed to determine if free-phase residual petroleum hydrocarbon product and/or groundwater containing dissolved COIs are discharging to and impacting the sediments and/or surface water of the Willamette River (Gradient 2008). Work completed included installation of borings and monitoring wells, and quarterly monitoring of groundwater quality and residual product thickness.

C2.0 SITE SELECTION

This section summarizes the decision process that was followed to identify the subset of upland groundwater sites where there is confirmed or reasonable likelihood of a complete groundwater transport pathway for COIs associated with known upland groundwater plumes to reach TZW in the Study Area.

C2.1 INITIAL SITE CLASSIFICATIONS

During the initial stages of the RI/FS process, the LWG conducted a review of groundwater sampling data available from Oregon DEQ files for upland sites located between RM 2 to 11, including sites bordering the river and sites with documented groundwater plumes in certain areas up to approximately 0.5 mile inland from the river (GSI 2003a). This review identified 113 sites, which were initially categorized according to their likelihood to represent a potential source of COIs to Portland Harbor via the groundwater transport pathway. The initial site categorization was presented in GSI (2003a) and was updated in the draft GWPA Technical Memorandum (GSI et al. 2004), submitted to USEPA on July 12, 2004.

The 113 upland sites were categorized as follows:

- **Category A** – Category A included 21 sites where COIs in groundwater have been confirmed to, or have a reasonable potential to, discharge to the river. All Category A sites were considered for inclusion in the GWPA. Representatives of USEPA, DEQ, and the LWG met on January 7, 2005, to review the 21 Category A sites and identify a subset of high-priority sites that would be carried forward into the site-specific scoping process for the GWPA. This review considered several factors, including the nature and extent of upland groundwater plumes, the presence or absence of detectable levels of upland groundwater COIs in nearshore wells, the presence or absence of NAPL in nearshore wells and/or in shoreline seeps, site-specific hydrogeological conditions (including stratigraphic evidence and/or direct observations of preferential flow paths, springs, or seeps), and the potential role of infrastructure (e.g., storm drain lines and other outfalls) in creating possible preferential flow paths. Based on this review, USEPA, in consultation with DEQ's upland site managers, selected 12 high-priority sites for which sufficient evidence of a complete groundwater transport pathway to the LWR existed to carry them forward into the site-specific scoping process for the Round 2 GWPA. The 12 high-priority Category A sites are shown on Figure C1.3-1 and listed below:
 - EOSM
 - Time Oil Northwest Terminal
 - Schnitzer Investment Corporation (Premier Edible Oils site)
 - Kinder Morgan Linnton Terminal

- ARCO Terminal 22T
- ExxonMobil Oil Terminal
- Gasco
- Siltronic
- Rhone Poulenc
- Arkema
- Willbridge Bulk Fuels Terminal
- Gunderson.

USEPA and DEQ determined that there was insufficient evidence to conclude that groundwater plumes associated with the remaining nine Category A sites were migrating to the Study Area, and these sites were eliminated from further evaluation in the GWPA.⁵

- **Category B** – Category B included 83 sites for which the potential for groundwater COIs to reach the river could not be confirmed based on available data. Category B sites were referred to Oregon DEQ for possible further evaluation of the potential for groundwater-related COIs to discharge to the river. During GWPA planning, Oregon DEQ did not identify a need for further evaluation in the RI/FS process of potential upland groundwater plume transport to the LWR at any Category B sites. Thus, none of the Category B sites were carried forward into the GWPA.
- **Category C** – Category C included nine sites where available site-specific groundwater data indicated at the time of GWPA scoping that groundwater COIs either are not present or are not likely to reach the river. Category C sites also were not evaluated further in the GWPA.

C2.2 SELECTION OF GWPA STUDY SITES

A further, more detailed review of available data was conducted for each of the 12 Category A sites that were carried forward into the scoping phase of the Round 2 GWPA by the LWG. The following criteria were established to determine an appropriate course of action for each of the 12 high-priority Category A sites shown in Figure C1.3-1::

- Criterion 1:** Existing offshore groundwater sampling data indicate that a potentially complete transport pathway exists for groundwater COIs to reach the transition zone.

⁵ The nine Category A sites that were not carried forward for the GWPA were McCall Oil; McCormick & Baxter; UPRR Albina Railroad; Port of Portland Terminal 4, Slip 3; Cascade General; Triangle Park; Foss Maritime; Mar Com; and Marine Finance.

- Criterion 2:** Existing shoreline sampling data from groundwater wells or seeps indicate a reasonable likelihood of a complete transport pathway for groundwater COIs to reach in-river exposure points.
- Criterion 3:** Existing observations of NAPL seepage to the river indicate that a complete transport pathway may exist for groundwater COIs to reach in-river exposure points.
- Criterion 4:** Shoreline groundwater seeps containing COIs are known to be present and represent a potentially complete exposure pathway for human receptors.

Each of the 12 high-priority Category A sites was evaluated against the site inclusion criteria described above. Sites that met one or more of the above inclusion criteria were included in the GWPA program. Sites for which insufficient data were available to determine if any of the inclusion criteria are met were referred to Oregon DEQ for additional uplands groundwater characterization (to be conducted by the upland party under DEQ oversight) to support a determination of whether in-water investigation of the groundwater transport pathway would be needed to support the RI/FS.

Based on the screening against these criteria, USEPA and DEQ determined nine of the 12 high-priority Category A sites were to be included in the GWPA. The three sites which were not included in the GWPA are EOSM, Time Oil Northwest Terminal, and Schnitzer Investment Corporation (Premier Edible Oils site). Complete summaries for each of these nine GWPA sites, including general background, hydrogeology, and the nature and extent of COIs in groundwater, are presented in Appendices A-1 through A-9 of the SAP (Integral et al. 2005). A site-by-site summary of the inclusion criteria evaluation is presented in Table C2.3-1 of this appendix, and specific discussion of the relevant characteristics of both included and excluded sites is provided below.

C2.2.1 High-Priority Sites Included in the Groundwater Pathway Assessment

The following discussion briefly summarizes individual site characteristics that led to inclusion in the GWPA.

C2.2.1.1 Kinder Morgan Linnton Terminal

The Kinder Morgan Linnton Terminal was included in the assessment based on Criterion 3, NAPL seepage to the river. A nearshore NAPL plume is present at the terminal, and floating product has been observed at thicknesses of 0.5 to 1 ft in shoreline wells. Shoreline seepage of NAPL has been observed along the waterfront near the access walkway for the southernmost dock. An Interim Remedial Action Measure (IRAM) Area Containment System is currently in place to address the southeastern extent of the NAPL plume, in the area of the NAPL seepage.

C2.2.1.2 ARCO Terminal 22T

ARCO Terminal 22T met two of the site inclusion criteria. Historical releases of petroleum products have resulted in a nearshore accumulation of LNAPL floating on the water table and a nearshore dissolved-phase petroleum plume. Wells and borings at the top of the shoreline indicate a reasonable likelihood of a complete transport pathway to the river for polycyclic aromatic hydrocarbons (PAHs) and metals (Criterion 2). Additionally, while the product recovery system generally contains the LNAPL discharge, incidences of LNAPL seepage to the river have been observed (Criterion 3).

C2.2.1.3 ExxonMobil Oil Terminal

The ExxonMobil Oil Terminal was included in the GWPA based on Criterion 2, as sampling data from shoreline wells at this site indicate a complete groundwater transport pathway for metals (e.g., lead and zinc) to in-river exposure points. While NAPL has historically been present at the terminal, a product recovery system is currently in place, and NAPL has only been observed in trace amounts since 2001.

C2.2.1.4 Gasco

The Gasco site was also included based on Criterion 2. Petroleum-related compounds, including benzene, toluene, ethylbenzene, xylenes (BTEX), and PAHs, were present in groundwater samples collected in 2004 from wells at the top of the embankment adjacent to the river. Groundwater and TZW samples collected during a 2006/2007 offshore investigation at the site demonstrated that the groundwater pathway is complete (Anchor 2008). While tar and oil are present within soil and groundwater across the southern and southeastern portions of the site, particularly in the area of the former tar ponds, a recent NAPL investigation concluded that the DNAPL is not currently discharging and has not in the past discharged to the Willamette River sediments offshore of the Northwest Natural portion of the Gasco site (Hahn and Associates 2005). The investigators based that conclusion on a lack of connectivity between oil-saturated soils within the alluvial water-bearing zone beneath the upland portion of the site and the oily or tarry sediments within the river.

C2.2.1.5 Siltronic

Two site inclusion criteria was met at the Siltronic site. First, Geoprobe[®] sampling data demonstrate the presence of site chemicals in the offshore groundwater, including halogenated volatile organic compounds (HVOCs), methyl-tert-butyl ether (MTBE), BTEX, and naphthalene (Criterion 1). The presence of these same chemicals in shoreline monitoring wells also indicates a reasonable likelihood of a complete groundwater transport pathway from the site to the river (Criterion 2). DNAPL (oil) has been identified near the shoreline at this site at depths of 110 to 125 ft bgs, but no subsurface NAPL seepage to the river has been observed, probably due to the depth of the plume. Although occasional observations of iridescent blooms and sheens have been observed offshore from Siltronic, it is uncertain whether these blooms and sheens are the result of historical direct discharges to the river (and resulting sediment impacts) or subsurface NAPL seepage.

C2.2.1.6 Rhone Poulenc

The Rhone Poulenc site satisfied two of the site inclusion criteria. Groundwater COIs, including HVOCs, insecticides (e.g., dichloro-diphenyl-trichloroethane [DDT]), herbicides (Silvex, 2,4-D), metals, and dioxins/furans have been detected in groundwater samples from nearshore wells downgradient of the site (Criterion 2). Rhone Poulenc is conducting additional work to investigate whether detections of insecticides as well as dioxins and furans are accurate (AMEC 2007, AMEC 2008a). In addition, contaminated groundwater infiltration into stormwater lines, which discharge to City Outfall 22B, has resulted in a surface expression of groundwater containing constituents from sites in the Doane Lake area as a small stream at a potential human use beach area on BNSF property downgradient of the site (Criterion 4). Detectable concentrations of site-related chemicals (e.g., 1,2-dichlorobenzene, Silvex, 2,4-D, DDT, dieldrin, dioxin/furans, and others) were found in samples collected from the outfall discharge (AMEC 2009).

C2.2.1.7 Arkema

Criteria 1 and 2 were met at the Arkema site. Site chemicals, including chromium, perchlorate, DDT, monochlorobenzene (MCB), and furan congeners, have been detected in groundwater samples from nearshore wells and in unfiltered water samples collected from in-water Geoprobe borings. (The unfiltered Geoprobe samples may be significantly high-biased by the introduction of sediment particulates during sampling; see Section C3.0.3.) While MCB is present upland as DNAPL, the DNAPL is distributed in the form of ganglia or microglobules coating soil particles. DNAPL ganglia and coatings were shown to thin at the nearshore margin of the Arkema site (ERM 2006a), and sampling in nearshore sediments did not identify any DNAPL migration pathways (Integral 2003). Therefore, the evidence indicates that DNAPL is not migrating offsite.

C2.2.1.8 Willbridge Bulk Fuels Terminal

The Willbridge Bulk Fuels Terminal also fulfilled two of the site inclusion criteria. Petroleum-related chemicals have been found in shoreline wells (e.g., PAHs and metals; Criterion 2). In addition, LNAPL seepages to the river have been observed at the municipal sewer outfall on the ConocoPhillips property and at the ConocoPhillips/Chevron property line (Criterion 3). NAPL seepage has been observed historically in the vicinity of the outfall from the 60-inch storm drain pipe located upstream of the docks. A cutoff wall was installed in 2002 and has been successful at eliminating NAPL seepage from this location. A project to line the storm drain is scheduled for summer 2009. A second cutoff wall, extending 200 ft along the river, was installed in 2006, cutting off seeps in the area of a former 27-inch outfall and the Holbrook Slough.

C2.2.1.9 Gunderson

The Gunderson site was included in the GWPA based on Criterion 2, as shoreline data at this site indicate a reasonable likelihood of a complete transport pathway for groundwater COIs to reach in-river exposure points. Metals (e.g., lead, zinc, chromium, and copper) and HVOCs, including trichloroethane (TCA) and its degradation products, have been

found in shoreline wells in Area 1, downgradient of the former Dip Tank Area. Metals (e.g., lead and chromium) have also been found in wells located along the riverbank in Area 3.

C2.2.2 High-Priority Sites Excluded from the Groundwater Pathway Assessment

Two of the high-priority Category A sites—EOSM and Time Oil Northwest Terminal—were found to not meet any of the site inclusion criteria and therefore were not included in the Portland Harbor GWPA field investigations. At PEO, the LWG, USEPA, and DEQ concurred that uplands characterization had been performed at the time of the GWPA to determine whether or not a groundwater transport pathway from the upland site to the river was complete or reasonably likely to be complete. As a result, during the scoping process for Round 3 investigations, USEPA and DEQ determined that any further evaluation of groundwater transport from the PEO site to the LWR would be conducted separately from the RI under DEQ's Joint Source Control Strategy (JSCS) program. These decisions were finalized during a July 12, 2007 meeting of the senior USEPA, DEQ, and LWG managers on Round 3B scoping.

Relevant background information for these three sites, available as of the June 2, 2008 RI data lockdown date, and the basis for excluding these sites from the GWPA are discussed in Attachment 1 to this appendix.

Additionally, none of the other nine sites that were initially classified as Category A, but that were not included in Round 2 GWPA field investigations for the reasons discussed above, was identified by USEPA and DEQ during the Round 3 scoping process as warranting inclusion in Round 3 GWPA field investigations. As with PEO, USEPA and DEQ determined that any future evaluation of the groundwater transport pathway to the LWR at any of these nine sites to the LWR would be conducted separately from the RI under the DEQ's JSCS program.

C3.0 SITE-SPECIFIC ASSESSMENT OF THE GROUNDWATER PATHWAY

This section presents the findings of the GWPA investigations conducted offshore of the nine TZW study sites as part of the Portland Harbor RI, as well as relevant data from site-specific investigations conducted by upland parties offshore of certain GWPA study sites. The intent of this section is to describe the groundwater pathway in sufficient detail to assess whether COIs associated with known upland groundwater plumes are discharging to the Study Area, thus creating a complete transport pathway for groundwater COIs to reach the groundwater-surface water transition zone in Study Area sediments.

The GWPA investigations conducted offshore of the nine study sites consisted of two primary elements: 1) identification of groundwater discharge zones within the river, and 2) sampling and analysis of TZW and collocated sediments for target COIs.

C3.0.1 Discharge Mapping

The groundwater discharge mapping element of the GWPA field investigation involved several methods of obtaining physical measurements to support the identification of groundwater discharge zones at the nine study sites. These methods included measurements of TZW temperature and conductivity using the Trident probe, observation and description of surface sediment texture, and measurements of flux across the sediment-water interface using seepage meters.

The Trident probe is a direct-push device equipped with probes that provide direct *in situ* measurements of TZW temperature and conductivity. These probes were calibrated daily in the field. Differences in temperature between TZW and surface water were measured and recorded, and trends and anomalies in these measurements were used as a line of evidence to identify areas of potential groundwater discharge. Temperature accuracy is reported by the manufacturer to be 0.001°C, with a resolution of 0.00025°C. (Conductivity measurements did not develop into a useful line of evidence for discharge mapping and are not discussed here.) Interpretation of Trident temperature results requires consideration of tidal influences, sediment texture, and stratigraphy. Because of tidal influences on the system, flux at the sediment-water interface can alternate between positive and negative over the course of each tidal cycle. While groundwater discharges to the river are typically expected to be higher in sandy versus silty sediments, reversal of the hydraulic gradient during high tide may also drive more surface water into sandy areas during tidal cycles. The resulting mixing can reduce the temperature contrast between TZW and surface water in coarser-grained materials. The effect of tidal mixing on transition-zone water temperature, however, is counterbalanced by the net groundwater flux to the river. Thus, Trident probe temperature measurements may be used to identify areas of relatively higher and lower discharge in coarse-grained sediments. Areas of higher discharge will generally exhibit greater temperature differences relative to other measurements in areas of lower discharge. Transition-zone temperature data in silty sediments should be interpreted more cautiously, anticipating

that tidal mixing effects are reduced in zones of lower hydraulic conductivity. These considerations informed the interpretation of the Trident probe temperature measurements in the discharge mapping effort and in the delineation of groundwater discharge zones in subsequent sections of this report.

Qualitative observations of surface sediment texture were performed (by “feel”) as the Trident probe was advanced at each discharge mapping location. Specifically, the operators were able to distinguish clearly between sand and silt, and, to a lesser degree, between silty sand and sandy silt. These qualitative observations were confirmed by sediment grab samples collected using a Ponar-type sampler at a 10 percent subset of the Trident probe mapping locations, and by observations of sediment that adhered to the probe upon removal. Sediment texture mapping was also supplemented by available sediment texture descriptions from Round 1 and Round 2 surface sediment samples. An important caveat is that surface sediment textures may not reflect the underlying stratigraphy. Sediment texture information is interpreted in conjunction with other lines of evidence—including upland and in-water stratigraphy, Trident probe temperature mapping, seepage meter measurements, and spatial patterns in TZW chemistry—in the delineation of groundwater discharge zones in subsequent sections of this report.

Measurements of groundwater flux were performed using ultrasonic-type seepage meters, which recorded continuous measurements of positive flux (net discharge from the transition zone to the surface water) and negative flux (net recharge from the surface water to the transition zone) at the sediment surface. Seepage meters were deployed for a minimum of 24 hours to record flux over at least one complete tidal cycle and allow for averaging of results to calculate net daily flow rates. Field replicates of discharge/recharge measurements were not collected. Detailed seepage meter measurement results are presented in the TZW FSP addenda (Integral 2006a, 2006b). Based on manufacturer and operator experience, these instruments are generally considered sensitive to roughly 1 cm/day. Seepage meter results are considered representative of discharge/recharge conditions at the location and time of the measurement. Discharge/recharge conditions may vary spatially as a function of local differences in stratigraphy, sediment texture, aquifer hydraulic properties, and hydraulic gradient. Discharge/recharge conditions may also vary in time as a function of river stage, tidal influences, and upland groundwater elevations and gradients. All Round 2 seepage meter measurements were performed in summer and fall, a period when river flows and stages are relatively low, to increase the likelihood that positive groundwater discharges to the river would be recorded.

These combined lines of evidence were interpreted to estimate zones of probable groundwater discharge associated with each of the nine sites. Additionally, the geochemical signatures, based on major ion composition, of TZW were compared to the geochemical signatures of upland groundwater and river water to assess if the groundwater discharge zones bear a unique geochemical signature from zones where low-to-no groundwater discharge is taking place. In addition, chemical data for a representative selection of COIs in groundwater, TZW, and sediment were compared in

zones of active groundwater discharge to zones where low-to-no groundwater discharge is taking place to evaluate if higher concentrations of these chemicals occur in sediments and TZW in areas where groundwater is discharging.

C3.0.2 TZW and Sediment Sampling and Analysis

A total of 155 shallow (<38 cm below mudline [bml]) and 34 deeper (38–150 cm bml) TZW samples were collected during the GWPA pilot study and 2005 TZW sampling program. Offshore of each of the nine study sites, one or more replicate TZW sample was collected using both peepers and the Trident, for a total of 34 replicate samples. Additionally, 31 TZW samples were collected offshore of the ARCO and Arkema sites during the 2004 GWPA pilot study. All of these samples were collected with the Trident or small-volume peepers. Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set offshore of each study site (including LWG data and non-LWG data collected by Gasco and Siltronic).

A total of 34 surface sediment samples were collected during the TZW sampling program to supplement the Round 1, Round 2, and Round 2B sediment data for each site. These data were added to the sediment database, which was then used to provide sediment data in support of the TZW data analysis. Detailed documentation of field sampling activities and locations is provided in the field sampling report (FSR; Integral 2006e). Complete TZW and sediment chemistry analytical results are presented in the site characterization and risk assessment (SCRA) database and are therefore not reproduced in this appendix.

As described in the Transition Zone Water and Sediment Data Validation Technical Memorandum (Appendix A to Integral 2006f), the replicate samples met established control limits for relative percent difference (RPD) for all samples and analytes. For additional insight on the reproducibility of the sampling tools, the replicate results were analyzed statistically by calculating the intraclass correlation coefficient (ICC)⁶ and the Pearson's correlation coefficient⁷ for all analytes. The Pearson's correlation coefficient (r) is a measure of systematic correlation between paired values from two data sets; values of r approaching 1 indicate very good correlation. The Pearson's correlation coefficient does not, however, provide information on systematic bias between the two data sets. In contrast, the ICC (ρ_i) is a combined measure of reproducibility and bias.

⁶ The ICC (ρ_i) is a measure of the reproducibility of replicate results. Specifically, ρ_i equals the ratio of the between-analyte variance to the sum of the between- and within-analyte variance. The ICC is used for pairs where designation as the dependent or independent variable is arbitrary. Specific applications include comparison of tests of the same subject by two judges or two methods and comparison of split sample laboratory results (Rosner 1995).

⁷ The Pearson (product moment) correlation coefficient (r) is the ratio of the covariation between the analyte concentrations in the two replicate samplers to the amount of covariation that would exist if the samplers had a perfect positive correlation. It should be noted that the Pearson correlation coefficient does not reflect system bias. Therefore, a good Pearson-type correlation does not necessarily indicate that the replicates are close to each other in value; instead it indicates that the ratio between the replicates is consistent. In other words, in interpreting results, it should be understood that a consistent bias, such as a 2:1 ratio between data sets, will give a good Pearson-type correlation.

The following ranges for the ICC values are considered standard for interpreting results (Fleiss 1986):

- $ICC \geq 0.8$ indicates excellent reproducibility
- $0.4 \leq ICC < 0.8$ indicates fair to good reproducibility
- $ICC < 0.4$ indicates poor reproducibility.

The results of these analyses are provided in Table C3.0-2. The replicate analysis results show excellent reproducibility, with the Pearson's correlation coefficient greater than 0.91 for all pairs and the ICC greater than 0.94 for all but 2 pairs. (The power grab pair at GS04-A had an ICC of 0.76, and the Trident 30-cm pair at EM03-A had an ICC of 0.74, both of which still show good reproducibility.)

The overall excellent reproducibility of the sampling results provides confidence in the representativeness of TZW and sediment samples collected by the Trident, peepers, and power grab tools. Additionally, these results provide some insight into local spatial variability. For the peepers, replicate samples were collected by deploying separate peepers at a distance of a few feet from the original samples. Given the excellent reproducibility observed for the peepers, there is some indication that the TZW quality does not vary significantly at the scale of several feet. The reproducibility of the power grab results suggests the same conclusion. In the case of the Trident replicates, the replicate samples were collected from the same deployment (i.e., the Trident probe was not moved). Therefore, the excellent reproducibility provides confidence in the continuity of sample composition over the duration of Trident sampling, including large sample volumes.

C3.0.3 Filtration of TZW Samples

Of the two general types of sampling tools utilized to collect TZW samples in the Study Area, push probes and small-volume peepers (peepers), filtration of samples is an important issue for push probes. The peeper samplers used in the LWR investigation are passive, equilibration-type samplers that have a $\sim 5 \mu\text{m}$ Teflon membrane in place between the sample space and the sediment/pore-water matrix. As such, the peeper samplers are not expected to mobilize and collect particulate material (though mobile colloidal material within the system would be collected by these samplers, and is considered representative of the mobile mass of contaminants in TZW). In contrast, push probe samplers are active samplers, collecting TZW by means of negative pressure from a peristaltic pump, potentially mobilizing particulate material from the sediment matrix in the pumping process. Available information about the effects of filtration of push probe samples on the representativeness of the TZW analytical results is discussed below, considering filter material, colloids, sampling protocols, and collocated filtered and unfiltered analytical results.

C3.0.3.1 Filter Material

One potential concern about use of filtration in sampling of metals and hydrophobic contaminants is that the dissolved contaminants in the sample will sorb to the filter material and be lost from the sample, thereby obscuring the truly mobile concentration of chemicals in the sample. For the filtration material used in TZW sampling at the nine study sites, sorption to the filter media is not expected to be an issue resulting in negative sampling bias. A literature review of the Versapore filter material used in the TZW push probe sampling (white acrylic copolymer coating over a nonwoven substrate) indicates that the filter material has been tested and applied successfully for use in environmental sampling of low-concentration inorganic contaminants (Gaillard et al. 1986; Magaritz et al. 1989; Ronen et al. 1987a; Geotech 2004) and organic contaminants (Ronen et al. 1987b; Krajenbrink et al. 1988; Kaplan et al. 1991; Shati et al. 1996; Laor et al. 2003).

C3.0.3.2 Colloids

Another consideration in assessment of the mobile fraction of contaminants (particularly metals and hydrophobic organic chemicals) is the role of colloids. Colloids are organic and/or inorganic particles present in many natural and anthropogenically influenced aqueous systems and are defined primarily by their size and corresponding physical behavior. Colloids range in size from <1 nm to 1 μm in diameter (Lyklema 1991) and tend to remain dispersed in water (behavior dominated by Brownian motion as opposed to settling), are subject to complex transport behavior,⁸ and are not filtered easily (Lyklema 1991). Because colloids can be mobile in water within a sediment matrix, they can increase the “apparent dissolved concentration” of hydrophobic chemicals or metals in the aqueous phase. Contaminants associated with/sorbed to mobile colloids should be considered part of the mobile fraction in an aqueous sample. As such, it is important to consider whether colloids could be removed in the filtration process, potentially resulting in a negatively biased estimate of the truly mobile chemical fraction.

For the unfiltered push probe samples collected in the Round 2 GWPA, there is no concern about loss of colloids by filtration (though non-mobile larger particles could also be collected). Likewise, with a pore size of $\sim 5 \mu\text{m}$ on the peeper membranes, the peeper samplers would be expected to collect colloids over the entire colloid size range of 1 nm to 1 μm (Lyklema 1991) via diffusion across the membrane (without concern of collection of non-mobile fraction). Finally, with a 0.45- μm filter size for the filtered push probe samples, any larger colloids (0.45 to 1 μm in diameter) may be excluded from these samples.

Some insight into the potential for filtration to result in negative sampling bias can be gained from a comparison of approximately collocated peeper and push probe samples, which were collected at sampling locations offshore of the Arkema and ARCO study

⁸ Mobile colloids (and any associated/sorbed contaminants) are subject to sorption/desorption kinetics through the sediment matrix, potentially slowing their progress relative to water. Conversely, colloids can travel faster than a conservative groundwater tracer in some cases due to a size exclusion effect (Enfield and Bengtsson 1998).

sites during the TZW pilot study. Although the small number of approximately collocated samples does not support a rigorous statistical analysis, the available results were compared in a limited inter-method analysis, presented in Round 2 TZW FSP (Integral 2006d). A more general review of the non-collocated peeper and push probe results across the study sites shows that peeper concentration ranges are generally similar to the filtered push probe samples for metals and hydrophobic chemicals (see Figures C3.1-7b, C3.1-7c, C3.2-7b, C3.2-7c, C3.2-7d, C3.4-8c, C3.4-8g, C3.5-9b, C3.6-8b, C3.6-8d, C3.7-7b, C3.7-7d, C3.7-7e, C3.8-8b, C3.8-8c, C3.8-8d, C3.8-9c, C3.8-9d, C3.8-9e, C3.9-8c, C3.9-8d, and C3.9-8e), with a few exceptions of higher and lower relative peeper concentrations for various chemicals at various sites. There are a variety of possible explanations for these observed variations, including the sample tool selection approach⁹ and the fact that these are comparisons of non-collocated samples. Without additional information, it cannot be determined definitively whether any colloids in the 0.45- μ m to 1- μ m size fraction might contribute significantly to the mobile contaminant fraction in TZW at any of the study sites, though there is no clear indication that they are from the existing data set.

C3.0.3.3 Sampling Protocols

Push probe sampling protocols were developed to minimize entrainment of non-mobile particulate matter in push probe sample collection; however, mobilization of even a small amount of particulate material can lead to significantly elevated sample concentrations, particularly for metals and highly hydrophobic organic chemicals¹⁰ (e.g., pesticides and HPAHs). To minimize the entrainment of particulate material during push probe sampling, standard well sampling procedures were followed. Specifically, pumping rates were kept at or below 0.1 L/min, and a volume equivalent to three times the pore volume of the tubing plus sampling probe was purged prior to sample collection. Push probe conditions, however, are not as controlled as in a properly constructed and developed sampling well. As such, it is recognized that particulate material may result in positive sampling bias in the unfiltered TZW samples collected by push probe. The following subsection presents and discusses comparison of analytical results for paired (collocated) filtered and unfiltered push probe samples to further evaluate this concern.

C3.0.3.4 Comparison of Collocated Filtered and Unfiltered Push Probe Data

For the locations where paired filtered and unfiltered TZW samples were collected by push probe, analytical results for metals, pesticides, and PAHs were compared to assess the difference between the filtered and unfiltered samples. These ratios are presented in Figures C3.0-1, C3.0-2, and C3.0-3 for metals, PAHs, and pesticides, respectively.

⁹ The sampling tool selection approach could introduce bias in terms of colloid content, though the direction of bias is uncertain. Specifically, peepers were generally used in areas of lower hydraulic conductivity sediments. Further, filtered data were only collected when sample volumes were adequate, suggesting conditions of highest relative hydraulic conductivity. Without additional information, it is difficult to speculate as to which condition might be expected to have more/any colloidal transport.

¹⁰ See Sections 6.2.1.1.1 and 6.2.1.1.2 of the main RI text for further discussion of literature and observed partition coefficients.

Symbols on the figures distinguish the TZW study sites. These figures indicate that unfiltered samples frequently exhibit significantly higher concentrations of metals, PAHs (particularly HPAHs), and pesticides as compared to their collocated filtered samples (i.e., the unfiltered concentrations frequently exceed the filtered concentrations by up to several orders of magnitude). The effect is greatest for metals (Figure C3.0-1), with the highest ratios associated with the Geoprobe-collected samples from the Gasco investigation (Anchor 2008). For PAHs, higher concentrations in the unfiltered samples are observed primarily for the higher-molecular weight PAHs (fluoranthene to benzo[g,h,i]perylene), likely due to the greater tendency of the HPAHs to sorb to particulate material. Finally, the DDx pesticides exhibit a similar upper range of unfiltered-to-filtered concentration ratios to that observed for HPAHs, extending to over two orders of magnitude above one. The very large magnitude of the concentration ratios in many of the paired unfiltered and filtered results for metals and hydrophobic organic chemicals suggests that many of the unfiltered results are positively biased by particulate material mobilized by the sampling process (i.e., not truly mobile in the sediment/pore water system). The potential for some small negative bias with respect to the mobile fraction in the filtered samples, due to removal of colloids in the 0.45- μ m to 1- μ m size fraction, also cannot be excluded.

C3.0.3.5 Filtration Effects Summary

In summary, the available evidence suggests that peeper and filtered push probe sample results are more representative of the mobile fraction of chemicals in transition zone water in the RI data set than are the unfiltered push probe results, although, as discussed above, the potential for some small negative bias with respect to the mobile fraction in the filtered samples, due to removal of colloids in the 0.45- μ m to 1- μ m size fraction, cannot be excluded. Specifically, there is no reason to expect sorption to the filter material or significant negative sampling bias due to loss of colloid-associated chemicals in peeper or filtered push-probe sampling.¹¹ Further, the paired (collocated) filtered and unfiltered push probe data suggest a greater likelihood that many of the unfiltered push probe samples contain sediment particulates mobilized by the sampling process, resulting in a significant high bias in the analytical results for metals and hydrophobic organic chemicals.

While this review of the data suggests that the peeper and filtered push probe samples are likely to be more representative of the truly mobile concentrations of chemicals in TZW, this appendix presents both filtered and unfiltered results on the maps and scatter plots presented in Section C3 of this appendix. Sampling methods are clearly identified on all figures to support transparent presentation of the findings.

¹¹ Note that, while there is no clear indication of negative sampling bias in filtered samples due to possible exclusion of colloids, the data set does not support a definitive assessment of the potential loss of colloids in the larger (0.45- μ m to 1- μ m size fraction) from filtered push probe samples.

C3.0.4 Multiple Lines-of-Evidence Evaluation

The assessment of the completeness of the groundwater transport pathway to the LWR offshore of each study site relies on the following lines of evidence:

- Nature and extent of COIs in upland groundwater and nearshore groundwater (where available)
- Upland and in-water subsurface stratigraphic information
- Upland groundwater flow patterns
- Trident probe discharge mapping results
- Surface sediment texture mapping
- Direct flux measurements using seepage meters
- Field screening analysis of TZW samples in select locations
- Analysis of spatial patterns in TZW chemistry, sediment chemistry, and upland groundwater chemistry
- Major ion analysis.

A uniform series of visualization and analysis tools is presented to develop these lines of evidence across each of the nine sites. These tools are described below as an introduction to their presentation and use on a site-by-site basis in this appendix.

- **Compilation of COI Concentrations in Upland Groundwater, TZW, and Sediments** – This table presents concentration data for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples. The COIs presented are not intended to be inclusive of all contaminants detected in upland groundwater, TZW, and sediment at a given site; rather, those presented are the select COIs that are considered diagnostic of the upland groundwater plume at each site and that are evaluated herein to assess potential groundwater transport pathways to the LWR at each site.
- **Site Overview and Cross-Section Location Map** – This figure supports introductory discussions of the site by presenting a plan view image of each site that highlights relevant site features (e.g., groundwater potentiometric surface, locations of remedial action systems), and the location of section lines for cross sections to be presented later in the report.
- **Distribution of NAPL and Select COIs in Upland Groundwater and Shallow TZW** – A series of figures is presented displaying the distribution of NAPL (if present) and select COIs in upland groundwater and shallow TZW (≤ 38 cm bml). The depiction of upland groundwater plumes on these figures is based on the most recent available upland groundwater sampling data that were collected prior to implementation of the GWPA. Upland data collected prior to, and closest in time with, the 2005 TZW sampling program were judged to be the most appropriate

data sets for the overall purpose of the GWPA, which was to assess whether complete transport pathways existed (at the time the GWPA was conducted) that allow COIs in upland groundwater plumes to discharge to the Study Area. It is acknowledged that the distribution of COIs in upland groundwater may have changed at some upland sites (e.g., as a result of implementation of source control measures) since the GWPA was conducted. All available TZW results (unfiltered Trident, filtered Trident, and peeper samples) are shown on the COI distribution figures. Symbols are used to differentiate the sample types. The COIs presented are not intended to be inclusive of all contaminants detected in upland groundwater at the site; rather those presented represent the occurrence, distribution, and concentrations of select COIs for a given site.

- **Stratigraphic Cross Section and Concentrations of Selected COIs in Nearshore Groundwater and Transition Zone Water** – One or more representative cross sections are presented for each site to illustrate the site stratigraphy and how it relates to groundwater flow. In addition, concentration data for select COIs in upland groundwater, nearshore groundwater (where available), and TZW are presented on the cross section to illustrate the distribution of COIs along the groundwater flow path.
- **Groundwater Discharge Mapping Results** – The results of the Trident probe discharge mapping (temperature and sediment texture mapping) and seepage meter measurements are presented to illustrate how these lines of evidence relate to potential groundwater discharge from the site.
- **Interpreted Groundwater Discharge Zones** – This figure presents the interpreted zones of groundwater discharge based on an evaluation of multiple lines of evidence. In addition, the locations where TZW and sediment samples have been collected at the site are provided to illustrate how these locations relate to the interpreted groundwater discharge zones.
- **Major Ion Analysis** – A Piper diagram is presented for each site to assess and compare the major ion signatures of site groundwater, site TZW, and Study Area surface water. The major ion composition data used to develop these figures, including calculations of charge balance, are presented in Table C3.0-3. Piper diagrams were prepared utilizing the Aquachem (Waterloo Hydrogeologic 2005) software package. Piper diagrams present two ternary diagrams, one for anions and a second for cations; the solution composition information contained in the two ternary diagrams is then projected onto a single diamond-shaped plot. The cation solution composition ternary diagram is constructed using the concentrations (in milliequivalents per liter [meq/L]) of Ca^{2+} , Mg^{2+} , and the sum of Na^+ and K^+ . The anion solution composition ternary diagram is constructed using the concentration (in meq/L) of Cl^- , SO_4^{2-} , and HCO_3^- . If HCO_3^- was not directly measured, then alkalinity and pH were used to estimate solution composition, using the PHREEQC model integrated into Aquachem. To facilitate comparisons between sites, a common, linear TDS scale is used for the symbol size on all of the site-specific Piper diagrams except for Rhone Poulenc and

Arkema, for which a logarithmic scale is used due to the larger variability in TDS at those two sites.

In addition to the individual Piper diagrams prepared for each of the nine study sites, Piper diagrams comparing the major ion composition of upland groundwater, TZW, and Study Area surface water across all nine sites have been prepared (Figures C3.0-4 and C3.0-5). For readability, the data shown on these figure have been broken down into four Piper diagrams: Upland groundwater (differentiated by site) and upland groundwater (differentiated by impacted versus unimpacted groundwater) are shown on Figure C3.0-4. TZW in low-to-no groundwater discharge zones and TZW in groundwater discharge zones are presented on Figure C3.0-5. Because the TDS content of upland groundwater and TZW varies over several orders of magnitude among the nine study sites, the symbols on the central, diamond-shaped plot are logarithmically scaled to TDS, with a symbol of 8-point size representing a TDS of 10 and a symbol of 50-point size representing a TDS of 1,000,000.

- **Concentrations of Select COIs in Groundwater, TZW, and Sediment** – These figures compare the range of COI concentrations measured in TZW and sediment in each of the groundwater discharge zones identified at the site. In addition, these concentrations are compared to the range in COI concentrations measured in nearshore upland groundwater samples and, where available, in-river groundwater samples (i.e., groundwater samples collected from the aquifer below the transition zone).

As appropriate, sections, figures and tables in the main text of the RI are referenced to support the GWPA analysis.

C3.1 KINDER MORGAN-LINNTON

The Kinder Morgan Linnton site is an operating bulk fuel storage facility located on the west bank of the Willamette River at approximately RM 4 (Figure C1.3-1). The site consists of approximately 15 acres located at 11400 NW St. Helens Road in the northeast corner of the community of Linnton, on a narrow strip of land between the Willamette River and the Portland Hills (Figure C3.1-1).

A detailed discussion of the Kinder Morgan Linnton site, including discussion of historical releases, source areas, and remedial measures, is presented the CSM site summary for Kinder Morgan Linnton (Integral and GSI 2004).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the Kinder Morgan-Linnton site are presented in Table C3.1-1.

C3.1.1 Nature and Extent of Contamination

Site soil and groundwater have been impacted by historical releases from the petroleum storage tanks, pipelines, and the current and historical product loading/unloading

locations. The historical releases of petroleum products have resulted in an accumulation of LNAPL floating on the water table (Figure C3.1-2a) and a dissolved-phase petroleum plume. Petroleum-related chemicals in groundwater include TPH, petroleum-related VOCs, and PAHs (Delta 2005a). In addition, several metals (e.g., arsenic, chromium, copper, and lead) are present in groundwater, some of which may be the result of redox changes in the aquifer caused by high organic carbon levels associated with petroleum releases.

Figures C3.1-2b–d present the distribution of total BTEX, total PAHs, and arsenic in groundwater and TZW, expressed as graduated symbols (or bubble plots). For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater sampling data collected prior to the 2005 implementation of the GWPA. Figures C3.1-3a–c present the concentrations of these same COIs along a representative stratigraphic cross section for the site. In general, the highest nearshore concentrations of total BTEX and total PAHs occur in shallow groundwater in the vicinity of the LNAPL (Figures C3.1-2a–c). Arsenic (and other metals detected in groundwater) are generally more broadly distributed across the site (Figure C3.1-2d).

C3.1.2 Completed and Ongoing Remediation Activities

As shown in Figure C3.1-1, an IRAM pump-and-treat system is in place at the Kinder Morgan Linnton site to address the LNAPL present near the shoreline on the upriver half of the site. This IRAM system began operation in July 2004 and is designed to recover LNAPL, control groundwater flow, and prevent groundwater/LNAPL seepage to the river by simultaneously extracting groundwater from the five recovery wells. According to the 2010 DEQ Milestone Report (DEQ 2010), the responsible party is preparing, in early 2011, an IRAM effectiveness evaluation and a focused feasibility study for barrier wall installation.

C3.1.3 Evaluation of Groundwater Discharge

The following presents an evaluation of multiple lines of evidence to interpret the extent of probable groundwater discharge at the Kinder Morgan Linnton site.

C3.1.3.1 Site Hydrogeology

Figures C3.1-3a–c present a representative cross section of the stratigraphy underlying the Kinder Morgan Linnton site, with the concentrations of total BTEX, total PAHs, and dissolved arsenic, respectively, observed in groundwater and TZW posted along the cross section. The cross section is oriented along the primary groundwater flow path to the river (Figure C3.1-1) and is representative of the stratigraphy across the site.

The site is underlain by two primary lithologic units—a surficial fill layer and an underlying alluvium. The surficial fill consists of sand and silty sand, and likely originated as dredged material from the Willamette and Columbia rivers. The fill layer ranges in thickness from 1 ft near the western property boundary to 35 ft near the river.

To the depth explored, the alluvium consists primarily of silt to sandy silt, although occasionally layers of sand, sandy gravel, or clayey silt are encountered.

A single unconfined aquifer underlies the site, with hydraulic connection between the surficial fill and underlying alluvium. Aquifer testing at the site resulted in a hydraulic conductivity (K) of 19.4 feet per day (ft/day; Delta 2005c), which is within the range of hydraulic conductivities typical of silty sand. In general, groundwater flow is expected to occur preferentially in the more permeable surficial materials (where present). Sediment cores collected offshore of the dock structure show a predominance of silt, with interbedded sands and a thin silty clay layer occurring in the subsurface downstream of the dock. The subsurface deposits observed in the offshore cores are generally consistent with the alluvial deposits identified beneath the upland surficial fill. As illustrated in Figures C3.1-3a–c, a portion of the surficial fill may daylight in the nearshore channel of the river, immediately adjacent to the seawall.

Groundwater has a general flow direction toward the river in the nearshore areas on a gradient of approximately 0.03 ft/ft (Figure C3.1-1). The groundwater potentiometric surface suggests a groundwater divide runs across the site, with groundwater at the downriver side of the site flowing to the north and groundwater flow at the upriver side of the site flowing to the west (Figure C3.1-1). The IRAM system is designed to recover LNAPL, control groundwater flow, and prevent groundwater/LNAPL seepage to the river by simultaneously extracting groundwater from the five recovery wells. Measurements of liquid (groundwater, LNAPL) levels indicate that pumping of the IRAM containment system has lowered the groundwater level immediately adjacent to the recovery wells; however, it is unknown if the system achieves complete capture of groundwater discharge from the site. A tiered timber seawall is also present over the entire shoreline of the site; however, it is not expected to bound groundwater flow.

The hydrogeologic data/information for the Kinder Morgan Linnton site suggest that any groundwater discharge from the site to the river is likely to occur in nearshore areas immediately adjacent to the seawall. Groundwater flux is expected to be greatest in the surface fill unit that intercepts the river, as this unit consists of generally more permeable materials than the underlying alluvium. However, discharge to the river is expected to be limited to some degree by the groundwater extraction instituted by the IRAM system.

C3.1.3.2 Groundwater Discharge Mapping Field Investigations

In 2005, the groundwater discharge mapping was performed at the Kinder Morgan Linnton site, in accordance with the Discharge Mapping FSP (Integral 2005c) to support the evaluation of active groundwater discharge zones associated with the site and to help focus the subsequent TZW sampling effort. Detailed results of the discharge mapping are presented in the SAP Addendum 2 (Integral 2006b).

The groundwater discharge mapping effort spanned the entire shoreline, extending both upstream and downstream of the site boundaries. In all, the Trident probe was deployed at 53 locations offshore of the Kinder Morgan Linnton site (Figure C3.1-4).

Additionally, ultrasonic seepage meters were installed for 24-hr periods at seven of the Trident locations.

C3.1.3.2.1 Surface Sediment Texture

Figure C3.1-4 presents the interpreted distribution of offshore sediment textures based on Trident observations and on materials observed in sediment samples collected offshore of the site. In general, the nearshore area to just beyond the dock area consists of silt extending from the upstream end of the site to cover roughly two-thirds of the shoreline. Over the downstream third of the site, clay was observed in the nearshore area extending downstream to the property line. The nearshore sediment textures are consistent with the projection of the alluvium unit observed in upland borings at the site. A sandy area is present in nearshore sediments immediately downstream of the site. Offshore of the site (i.e. past the dock structure, approximately at the break in the bank slope) the sediments trend to mixed sand and silts.

C3.1.3.2.2 Trident Probe Temperature Mapping

Figure C3.1-4 presents the Trident probe temperature profiling results. The Trident data indicate several general patterns. The clay-covered area, located within the northern portion of the dock structure and in the silt areas shoreward of the dock structure, showed generally minimal temperature signals (low temperature differences), with a few exceptions (KM15-A, KM8-A, KM10-A, and KM11-B). In response, seepage meters were placed at KM8-A and KM11-B. In the sandy area just downstream of the site, only KM2-E showed a strong temperature signal. To assess the sand and possible effect of mixing between groundwater and surface water in these coarser sediments, seepage meters were placed at KM1-B and KM2-E. Just offshore of the dock structure, Trident measurements show stronger temperature signals. This is consistent with observations in silty zones at other sites, including those observed during the pilot study, as reported in the Discharge Mapping FSP (Integral 2005c). To further evaluate this zone, seepage meters were placed at KM15-C and KM10-D. Finally, the mixed silt and sand zone farther offshore of the site showed some temperature variation, and a seepage meter was placed at KM12-D, where the temperature signals were relatively strong.

C3.1.3.2.3 Seepage Flux Measurements

Seepage meters were installed at seven of the Trident locations offshore of the Kinder Morgan site: KM1-B, KM2-E, KM8-A, KM10-D, KM11-B, KM12-D, and KM15-C. These seepage meter locations are designated as KMSEEP 1B, KMSEEP 2E, KMSEEP 8A, KMSEEP 10D, KMSEEP 11B, KMSEEP 12D, and KMSEEP 15C. As shown in Figure C3.1-4, average seepage fluxes were close to zero or slightly negative for all but one location: KMSEEP 8A. This location is immediately adjacent to the shoreline in an area of sandy fill material near the wooden seawall. Low net positive flow was also observed at KMSEEP 11B.

C3.1.3.3 Interpreted Zones of the Groundwater Discharge

The combined lines of evidence of the groundwater discharge mapping (including review of site stratigraphy, upland groundwater contours and concentrations, sediment texture,

Trident temperature results, and seepage meter results) suggest that the shallow groundwater discharge and any associated migration of upland groundwater COIs to the river are likely occurring primarily in the nearshore area adjacent to the LNAPL plume.

Figure C3.1-5 presents the approximate zones of groundwater discharge offshore of the Kinder Morgan Linnton site interpreted from these data and identifies one small, nearshore area as a groundwater discharge zone. This designation is based primarily on the seepage meter results at KMSEEP 8A (24-hr average seepage rate measurement of 4.8 cm/day) and the stratigraphic understanding of the site. This area is located directly off the area of the NAPL and in the area of previously observed seeps at the site (Integral et al. 2005). A portion of the groundwater flux in this area is captured by the IRAM system.

The remaining offshore area is designated as a low-to-no groundwater discharge zone based on the discharge mapping results (including six seepage meter measurements) and the stratigraphic understanding of the site. The nearshore sand and clay areas at the downstream end of the site, as well as the silty zone offshore of the dock area, do not show evidence of groundwater discharge. Seepage meter results also showed no evidence of groundwater discharge through the offshore mixed sand and silt areas, located closer to shore in the upstream area of the site (with the exception of the very low net positive flow observed at KMSEEP 11B).

C3.1.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

A total of seven TZW samples were collected from six locations at the Kinder Morgan Linnton site (Figure C3.1-1). Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the Kinder Morgan Linnton site. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from a target depth of 150 cm at one of the locations. The rationale for selection of the sampling locations was as follows:

- Samples were collected from four locations at the nearshore area adjacent to the LNAPL plume. These sampling locations are labeled R2-KM-1, KM-05A, KM-06-A, and KM-10-A.
- A sample was collected at KM-11-B, where there was a relatively strong temperature signal, and the seepage meter results showed a small, but positive average discharge.
- A sample was collected at location R2-KM-02, within the offshore zone of surficial mixed sand and silt, to evaluate whether there is a pathway of more conductive material that extends from this mixed zone upgradient to upland groundwater COIs. A paired sample at a depth of 150 cm was also collected at this location.

Results of the TZW analyses are presented in detail in RI Section 5. The following presents an evaluation of chemical concentrations in TZW, sediment, and surface water at

the Kinder Morgan Linnton site and how these data relate to the interpretation of groundwater discharge at the site.

C3.1.4.1 Major Ion Composition

Figure C3.1-6 presents the major ion composition of the TZW samples collected offshore of the Kinder Morgan Linnton site, and compares them to the major ion composition of river water samples collected at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are linearly scaled from 0 to 2,200 mg/L. Complete major ion composition data are not available for upland groundwater at the site. Table C3.0-3 presents the major ion concentration data and associated charge balance for the samples plotted in Figure C3.1-6. The charge balance achieved for the Kinder Morgan Linnton site TZW samples was typically ± 15 percent or less, with most samples being anion deficient (i.e., negative charge balance). This finding is likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis.¹² However, three TZW samples had charge balances ranging from ± 24 to ± 32 percent, suggesting a moderate imbalance in the measured cation/anion composition.

Both the TZW and the river water are predominantly calcium-carbonate waters; however, the river water shows a greater influence of sodium and chloride. TZW major ion composition is not significantly different between samples collected from the interpreted groundwater discharge zone and from the zone where low-to-no groundwater discharge is estimated to be taking place. These results suggest that the TZW major ion composition is more strongly influenced by geochemical interactions within the sediment pore space (e.g., mineral dissolution and precipitation, microbial processes) than by the degree of groundwater and surface water mixing in the transition zone. As a result, the major ion composition of the TZW at the Kinder Morgan Linnton site is not a good indicator of groundwater discharge.

C3.1.4.2 Distribution of COIs Relative to Groundwater Discharge Zones,

Figure C3.1-5 illustrates where the TZW and sediment sampling locations are situated relative to the interpreted zones of groundwater discharge. Figures C3.1-7a–c present the range of concentrations of select COIs observed in nearshore upland groundwater, TZW, and sediments in both the groundwater discharge zone and in the low-to-no groundwater discharge zone. These data are also presented in Table C3.1-1. The following summarizes the findings of this analysis:

- **BTEX (Figure C3.1-7a)** – Eight TZW samples from seven locations are available for total BTEX in TZW at the Kinder Morgan Linnton site: two samples from separate locations in the groundwater discharge zone and six samples from five locations in the low-to-no groundwater discharge zone. At one location in

¹² TZW is not in direct communication with the atmosphere. As a result, it is not uncommon for TZW samples to release carbon dioxide and move toward chemical equilibrium with atmospheric carbon dioxide during sample collection and processing.

the low-to-no groundwater discharge zone (R2-KM02), samples were collected at depths of 30 cm and 150 cm. The available data suggest that the concentrations are similar in samples from both the groundwater discharge zone and the low-to-no groundwater discharge zone, and are considerably lower than the range observed in nearshore upland groundwater. BTEX was detected in two of the eight TZW samples, at concentrations of 0.23 µg/L (R2-KM02; 30 cm) and 0.26 µg/L (R2-KM02; 150 cm); both of these locations were collected from the same station (at different depths) in the low-to-no groundwater discharge zone. BTEX was undetected in the other six TZW samples, all at a detection limit of 0.22 µg/L. BTEX was non-detect in the two sediment samples collected from the groundwater discharge zone. BTEX was also frequently non-detect in sediment samples from the low-to-no discharge zone; however, it was detected in four of 16 samples at concentrations ranging from 0.034 to 5.2 mg/kg. These data suggest that the groundwater discharge pathway is not complete for BTEX at the Kinder Morgan Linnton site.

- **Total PAHs (Figure C3.1-7b)** – The available, although limited, total PAH concentration data for the two TZW sample locations in the groundwater discharge zone offshore of Kinder Morgan Linnton are slightly higher than for the four TZW samples collected from the low-to-no groundwater discharge zone. However, the total PAH concentrations in all of the Kinder Morgan Linnton TZW samples are low (18.6 µg/L maximum) and are comparable to the lower end of the range of concentrations observed in upland groundwater. The PAH composition in TZW samples from the groundwater discharge zone is dominated by LPAHs (96 percent of total PAHs at R2KM01 and 84 percent at KM08A). The low-to-no groundwater discharge zone TZW samples show more variable PAH compositions (LPAH fractions of 26 percent at KM06A, 76 percent at R2KM02, 42 percent at KM10A, and 97 percent at KM11B). The PAH composition in upland groundwater from Kinder Morgan Linnton is dominated by LPAHs, with most samples containing >80 percent LPAH. Total PAH concentrations in the two sediment samples from the groundwater discharge zone are within the range of concentrations measured in sediment samples from the low-to-no groundwater discharge zone. While these observations suggest that total PAHs in upland groundwater may be migrating to the transition zone in the groundwater discharge zone offshore of Kinder Morgan Linnton, the concentrations in TZW are relatively low relative to upland groundwater concentrations. The presence of total PAHs in sediments from both the groundwater discharge zone and the low-to-no groundwater discharge zone suggests it is also possible that chemical partitioning to pore water from sediment may be contributing to the relatively low levels of total PAH measured in TZW samples.
- **Arsenic (Figure C3.1-7c)** – Arsenic concentrations observed in TZW samples from the groundwater discharge zone are comparable to the high end of the range of those measured in TZW from the low-to-no groundwater discharge zone. The arsenic concentrations in TZW from both of these zones are comparable to the concentrations observed in the upland groundwater. In support of the analysis

presented in Section C4.0, arsenic data were also compiled for “background” wells, which are located upgradient of known impacts to upland groundwater at several sites bordering the Study Area (see Section C4.1, Table C4.0-4). While the upper end of the arsenic concentration range in upland groundwater at the Kinder Morgan Linnton site exceeds the background range, the concentrations of arsenic observed in TZW offshore of the Kinder Morgan Linnton site are generally within the range for background groundwater wells. TZW arsenic concentrations in the groundwater discharge zone lie at the higher end of that range. Arsenic concentrations in the two sediment samples from the groundwater discharge zone are on the low end of the range of concentrations measured in sediment samples from the low-to-no groundwater discharge zone.

C3.1.5 Groundwater Pathway Assessment for the Kinder Morgan Linnton Site

Based on an integrated analysis of all of the lines of evidence presented in Section C3.1.3, a small nearshore area was identified where groundwater discharge occurs at the Kinder Morgan Linnton site. Other areas offshore of the site were identified as a low-to-no groundwater discharge zone, based on seepage meter measurements, Trident probe temperature measurements, sediment texture, and stratigraphic information. The available data suggest that the concentrations of PAHs in TZW are higher in the area identified as a groundwater discharge zone than in the low-to-no flow zone, but the TZW concentrations are substantially lower than upland groundwater concentrations. The average LPAH fraction of total PAHs in TZW samples from the groundwater discharge zone is 90 percent, which is similar to the LPAH fraction in upland groundwater samples. The LPAH fraction is 60 percent in TZW samples from the low-to-no groundwater discharge zone. Given the small sample counts in both the groundwater discharge zone (n=2) and the low-to-no groundwater discharge zone (n=4) any conclusions based on PAH composition with respect to upland groundwater plume transport of PAHs to the LWR are uncertain and must be viewed with caution. Concentrations of arsenic do not show any difference in concentrations inside or outside of the groundwater discharge zone, and are similar to levels in upland groundwater. A detailed evaluation of the occurrence of arsenic, barium, and manganese in TZW at the Kinder Morgan Linnton site is presented in Section C4.0.

The combined lines of evidence suggest some possibility that low levels of PAHs in upland groundwater may be migrating to the transition zone in the groundwater discharge zone offshore of the Kinder Morgan Linnton site. It is also plausible that partitioning to pore water from sediment is contributing to the levels of total PAH measured in TZW samples in both the groundwater discharge zone and the low-to-no groundwater discharge zone. BTEX was undetected in the TZW samples from the groundwater discharge zone; therefore, evidence is absent for a complete transport pathway for BTEX in upland groundwater to migrate to the transition zone. The available arsenic TZW data are consistent with observations in TZW samples collected at other GWPA sites in both active groundwater discharge zones and in low-to-no flow zones, indicating the absence

of a complete and significant transport pathway to the river for arsenic in groundwater at the Kinder Morgan Linnton site.

C3.2 ARCO

The ARCO site is an operating bulk fuel storage facility located on the western shore of the Willamette at approximately RM 4.9 (Figure C1.3-1). A detailed discussion of the ARCO site, including discussion of historical releases, source areas, and remedial measures is presented in the CSM site summary for ARCO (Integral 2007a).

The ARCO terminal houses 27 ASTs, a remanufacturing warehouse (not in use), office and shop buildings, and a truck-loading facility (Figure C3.2-1). The ASTs at the site contain gasoline, diesel, lube oil, and additives. The site also includes a wharf on the Willamette River with an associated building. An 800-ft concrete seawall is located along the river. Concrete riprap and rubble extend from the toe of the seawall to the approximate low-water line. To address concerns about possible LNAPL migration beneath the seawall during low-tide/low-stage conditions, a subsurface sheetpile seawall was constructed along the shoreline in 2007 (DEQ 2010).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the ARCO site are presented in Table C3.2-1.

C3.2.1 Nature and Extent of Contamination

During historical operations, occasional releases of product occurred from underground pipelines, tanks, and during product transfer and have resulted in an accumulation of LNAPL floating on the water table and a dissolved-phase petroleum plume. Petroleum-related chemicals in groundwater include TPH, petroleum-related VOCs, and PAHs (SECOR 2002; URS 2004a). In addition, several metals (e.g., arsenic, chromium, copper, and lead) are present in groundwater, some of which may be the result of redox changes in the aquifer caused by high organic carbon levels associated with petroleum releases and/or naturally occurring organic matter.

LNAPL has been observed in the shallow aquifer beneath two areas of the site and at the adjacent Linnton Plywood Association (LPA) property (URS 2004b); Figure C3.2-2a). The LNAPL is thickest in the area of the coarse-grained channel fill material. Figures C3.2-2b–e present the distribution of total BTEX, total PAHs, lead, and arsenic in groundwater and TZW, expressed as graduated symbols (or bubble plots).¹³ For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater

¹³ At many locations, groundwater samples were collected from multiple depths; some were significantly below the water table. The concentrations shown on Figures 3.3-2b–e are those measured in the shallowest samples (i.e., those nearest the water table) where concentrations tend to be the greatest. Note that URS believes that the TPH-diesel result collected from a depth of 64 ft at GP-5 (Table 1d, URS 2004a) is anomalous (Moody 2005, pers. comm.)

sampling data collected prior to the 2005 implementation of the GWPA. These chemicals were selected to represent overall groundwater conditions. Figures C3.2-3a–c present the occurrence of these chemicals along a representative stratigraphic cross section for the site.

The main part of the dissolved petroleum hydrocarbon groundwater plume is beneath and near the LNAPL source areas. Elevated dissolved metals concentrations closely mimic the TPH plume shape. To the north, the plume extends onto the LPA facility from a point on the property boundary approximately 120 ft west of the shoreline to a point along the shoreline approximately 100 ft north of the boundary (URS 2004b). Analytical results and field observations from borings on the LPA property indicate the presence of gasoline and diesel in soil and groundwater. The southern extent of the groundwater plume was evaluated against existing ARCO and ExxonMobil soil and groundwater data (URS 2004b). Although petroleum impacts on soil have been noted at the property boundary, concentrations of petroleum constituents in groundwater are relatively low in this area.

C3.2.2 Completed and Ongoing Remediation Activities

Figure C3.2-1 shows the approximate locations of the components of the remediation systems that are in place at the ARCO site. Between 1942 and 1945, ARCO constructed the concrete seawall adjacent to the Willamette River waterfront. The seawall was constructed to prevent shoreline erosion and was not designed as a specific remedial measure to minimize the discharge of groundwater contamination to the river (URS 2004a). From 1968 to the present, ARCO has initiated several process improvements to protect the river from contamination, including constructing a stormwater collection system and a product/groundwater recovery system to contain free product and prevent it from reaching the river (SECOR 2000). The seawall, coupled with the recovery system, largely prevents the LNAPL from discharging to the river. However, URS (2004a) found that it could be possible for LNAPL to discharge to the river when the river stage elevation and/or the oil/water interface drop below the base of the seawall. To address this concern and enhance hydraulic control of contaminated groundwater, a permanent sheetpile seawall was constructed along the ARCO shoreline in 2007 (DEQ 2010). The seawall and the recovery system also limit the migration of aqueous-phase COIs to the river with discharging groundwater. The ARCO seawall does not extend onto the LPA property, and, thus, lateral migration from the shallow alluvium to the river is not restricted in the same manner as it is at the ARCO property.

C3.2.3 Evaluation of Groundwater Discharge

The following presents an evaluation of multiple lines of evidence to interpret the extent of probable groundwater discharge at the ARCO site.

C3.2.3.1 Hydrogeology

Lithologic logs of materials collected during numerous site subsurface investigations provide a comprehensive picture of site stratigraphic features that influence groundwater

flow beneath the site. Figures C3.2-3a–c present a representative stratigraphic cross section for the site based on the upland stratigraphical interpretations obtained from URS (2004a, 2004b) and extended into the river based on sediment coring data collected during Round 2 of the RI field investigation (Integral et al. 2006). The general site stratigraphy from the ground surface downward consists of the following units (URS 2004a):

- **Recent Fill** – The surficial fill at the site consists of sand, sandy gravel and cobbles, gravelly sand, and some debris.
- **Pleistocene-Recent Alluvium** – The fill layer is underlain by alluvium. This deposit trends with depth from finer-grained silty materials to sandier materials, and generally forms two layers: an overlying fine-grained alluvium and an underlying sandy alluvium. The fine-grained alluvium is directly beneath the fill layer and consists primarily of fine-grained silts and lean clay with interbeds of silty sands. This layer is typically 10 to 15 ft thick. The underlying sandy alluvium consists of sandy material with silt interbeds and extends to the top of the CRBG. A west-east-trending, buried erosional channel is present beneath the middle of the site. This feature cuts into the fine-grained alluvium layer and has been filled with coarser channel-fill material (sand and gravel; URS 2004a). It is unclear if the channel cuts entirely through the fine-grained alluvium layer and into the sand alluvium below.
- **Columbia River Basalt** – The CRBG occurs at depths of between 40 ft bgs in the western part of the site and 70 ft bgs near the seawall (URS 2004a).

The shallow aquifer system beneath the site generally occurs in the fill layer, with the underlying fine-grained alluvial deposits, where present, acting as an aquitard. Within the shallow aquifer, groundwater flow toward the river is impeded to some extent by the seawall; however, the seawall is generally not keyed into the fine-grained alluvial layer (URS 2004a). The more permeable materials of the buried west-east erosional feature underlying the middle of the site represent a preferential pathway for groundwater flow.

The general direction of groundwater flow is east toward the Willamette River (Figure C3.2-1). Based on water levels measured in 2000, the hydraulic gradient is ~0.05 ft/ft, with flatter gradients of ~0.01 ft/ft occurring in the area of the coarse channel deposits. Aquifer testing completed at the site resulted in hydraulic conductivity estimates of 33–100 ft/day in the coarse-grained channel fill material, 0.5–2 ft/day in the fine-grained alluvium, and 1–2 ft/day in the sandy alluvium (SECOR 2002; URS 2004a).

C3.2.3.2 Groundwater Discharge Mapping Field Investigations

Groundwater discharge mapping was performed at the ARCO site during both the fall 2004 GWPA pilot study and the summer 2005 Round 2 GWPA field effort to help focus the subsequent TZW sampling. Combined, the two mapping efforts span the entire shoreline of the site. Trident temperature mapping and seepage meter results are summarized in Figure C3.2-4. Detailed results of the discharge mapping are presented in

SAP Addendum 2 (Integral 2006b). In all, 54 in-river measurements were made with the Trident probe (Figure C3.2-4). The Trident probe collected temperature and conductivity data above and below the sediment surface, as well as sediment texture information. Additionally, ultrasonic seepage meters were installed for 24-hr periods at seven of the Trident locations offshore of the ARCO site during the 2005 field effort.

C3.2.3.2.1 Surface Sediment Texture

Figure C3.2-4 presents the interpreted distribution of near-surface sediment texture based on the Trident probe work and sediment samples collected adjacent to the site. A narrow nearshore zone of sandy sediments extends across the entire length of the site, consistent with the projection to the river of the bottom of the surficial fill water-bearing zone that underlies the site. Beyond this zone, the surface sediments trend to mixed sand and silt, and then to silt farther offshore. The mixed sand/silt and silt zones are likely the expression of the alluvial deposit that underlies the fill water-bearing unit. The sand unit that underlies this deposit was not observed during either of the 2004 or 2005 investigations, but may daylight farther offshore.

C3.2.3.2.2 Trident Temperature Mapping

The results of the 2004 Trident work indicated temperature signals at locations ARC-03-B and ARC-06-B that could be indicative of groundwater discharge (Figure C3.2-4). These locations were selected for TZW sampling during the pilot study based on the Trident data and their position relative to the buried channel and the uplands LNAPL area. ARC-02-B was also selected as a pilot study sampling location with the objective of collecting information at a comparable distance from the shoreline, where a more typical temperature signal was observed (Figure C3.2-4). The 2005 ARCO Trident data displayed similar trends as those observed during the 2004 pilot study (Figure C3.2-4). Locations AR1-A, AR3-B, and AR5-B showed a fairly strong temperature signal, potentially indicating a higher relative groundwater discharge rate.

C3.2.3.2.3 Seepage Rate Measurements

Seven seepage meters were deployed at ARCO during the 2005 event, focusing primarily on the nearshore areas where the shallow water-bearing zone is likely to discharge to the river.¹⁴ Seepage meters were installed at four of the 2005 Trident locations offshore of the ARCO site: AR2-A, AR3-C, AR5-B, and AR7-B. The remaining three seepage meters were placed in the area evaluated during the 2004 pilot study, including one seepage meter placed at pilot study location ARC-06-B, where the temperature signal suggested groundwater discharge may be occurring. The seepage meter locations are designated ARSEEP 2A, ARSEEP 3C, ARSEEP 5B, ARSEEP 7B, ARSEEP 8, ARSEEP 9, and ARSEEP 10 (Figure C3.2-4).

¹⁴ Due to low river water levels at the time of both the 2004 and 2005 field events, the narrow nearshore sand zone was often dry or in very shallow water. As a result, at several locations, Trident probe and seepage meter measurements often could not be placed within the nearshore sand zone expected to be connected to the upland shallow water-bearing zone. Instead, measurements were taken as close to shore as reasonably feasible.

The average seepage flux measured at each location is summarized in Figure C3.2-4. Location ARSEEP 8, the only seepage meter that could be placed in the nearshore sand zone, displayed a high seepage rate (average 14.2 cm/day). Although somewhat lower, the seepage rate recorded in the mixed sand/silt at location ARSEEP 2A was also strongly positive (average 5.3 cm/day). The seepage rates recorded at the remaining five locations ranged, on average, from slightly positive to slightly negative, indicating that these locations are not areas of significant groundwater discharge.

C3.2.3.3 Interpretation of Groundwater Discharge Zones

The combined lines of evidence presented above suggest that shallow groundwater flow occurs primarily via the permeable, near-surface fill materials at the site and discharges to the associated permeable sediments present immediately adjacent to the site shoreline. A portion of the groundwater flow in the fill materials is impeded to some degree by the seawall and captured by the groundwater recovery system operated at the site. Based on an integrated analysis of all lines of evidence, two areas of nearshore groundwater discharge were identified at the ARCO site (Figure C3.2-5). Other areas offshore of the site were identified as a low-to-no flow discharge zone based on seepage meter measurements, Trident probe temperature measurements, sediment texture, and stratigraphic information.

C3.2.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

TZW samples were collected from seven locations during the TZW sampling event and from three additional locations during the pilot study. Sampling locations are shown on Figure C3.2-1, and Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the ARCO site. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from a target depth of 90 to 150 cm at two of the locations. Where possible, filtered samples were collected following collection of unfiltered samples. The rationale for selection of the sampling locations was as follows:

- Samples were collected from four locations (R2-AR-01, R2-AR-02, R2-AR-03, and R2-AR-04) in the nearshore sand zone offshore of the site to provide sample coverage in areas offshore of the primary zones of upland groundwater COIs of the site. A paired sample at a depth of 90 cm was collected at location R2-AR-02, where the highest seepage rate was recorded at the site.
- Samples were collected from three nearshore locations (AR-01-A, AR-02-A, and AR-04-B) in the sand and mixed sand/silt zones offshore of the northernmost LNAPL source area, immediately downstream from the site. Location AR-02-A is the position (ARSEEP 2A) where seepage meter results indicate significant discharge. Locations AR-01-A and AR-04-B are located upstream and downstream of AR-02-A. A paired sample at a depth of 150 cm was collected at AR-01-A.

C3.2.4.1 Major Ion Composition

Figure C3.2-6 presents the major ion composition for TZW and upland groundwater at the ARCO site, and compares these compositions to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are linearly scaled from 0 to 2,200 mg/L. Table C3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the ARCO site TZW samples was typically ± 15 percent or less, with most samples being anion deficient likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis.

Groundwater, TZW, and river water at the ARCO site are all predominantly calcium-carbonate waters; however, the river water shows a greater influence of sodium and chloride than is shown by the TZW and upland groundwater samples. TZW major ion composition is not significantly different in samples collected from the interpreted groundwater discharge zone than from samples collected from the zone where low-to-no groundwater discharge is interpreted to be taking place. Further, the upland groundwater major ion composition is generally similar to the TZW composition. These data suggest that the TZW major ion composition is influenced by geochemical interactions within the sediment pore space (e.g., mineral dissolution and precipitation, microbial processes) and that these processes are similar to those acting in the upland aquifer to establish the groundwater major ion composition. As a result, the TZW major ion composition is not strongly tied to groundwater discharge.

C3.2.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figure C3.2-5 illustrates where the TZW sampling locations, as well as the sediment sampling locations, are situated relative to the interpreted zones of groundwater discharge. Figures C3.2-7a–d present the range of concentrations of select COIs observed in nearshore groundwater and in TZW and sediments from the interpreted groundwater discharge zones and the low-to-no groundwater discharge zone. These data are also presented in Table C3.2-1. The majority of the TZW samples were collected from the low-to-no flow groundwater zone. Two TZW samples were collected from the downstream groundwater discharge zone; however, no TZW samples were collected from the other nearshore groundwater discharge zone identified at the site. The following summarizes the findings of this analysis:

- **BTEX (Figure C3.2-7a)** – BTEX concentrations were below detection in the shallow TZW samples collected from the downstream groundwater discharge zones. BTEX concentrations in TZW collected from the low-to-no groundwater discharge zone were frequently below detection and, when detected, were low (<2 ppb). Detected BTEX concentrations in all of the TZW samples were considerably lower than the range of concentrations in upland groundwater. BTEX was detected at low concentration (<0.1 ppb) in the sediment samples from the downstream groundwater discharge zone. BTEX concentrations in sediment

samples from the low-to-no groundwater discharge zone ranged from below detection to several hundred ppm.

- **Total PAHs (Figure C3.2-7b)** – Upland groundwater and TZW from the low-to-no groundwater discharge exhibited a similar range in total PAH concentration. Although limited to two samples, the total PAH concentration in the TZW samples from the downstream groundwater discharge zone was consistent with those measured in upland groundwater and TZW from the low-to-no groundwater discharge zone. Sediment total PAH concentrations exhibited a wide range in the low-to-no groundwater discharge zone. The sediment total PAH concentrations in the groundwater discharge zones were consistent with the range in the low-to-no groundwater discharge zone, although the two sediment samples from the downstream groundwater discharge zone exhibited concentrations at the upper end of the range observed in the low-to-no groundwater discharge zone.
- **Arsenic (Figure C3.2-7c)** – Arsenic concentrations were similar in upland groundwater and in TZW from both the downstream groundwater discharge zone and the low-to-no groundwater discharge zone. The upper range of the arsenic concentrations measured in upland groundwater and TZW from the ARCO site is somewhat higher than the arsenic concentrations in the background groundwater wells identified for the Study Area (see Section C4.0). Sediment arsenic concentrations were also similar between the two groundwater discharge zones, although the downstream groundwater discharge zone exhibited sediment arsenic concentrations at the upper end of the range of the sediment arsenic concentrations in the low-to-no groundwater discharge zone.
- **Lead (Figure C3.2-7d)** – Lead was below detection in the TZW samples collected from the downstream groundwater discharge zone. Lead, when detected, was present at low levels in TZW from the low-to-no groundwater discharge zone—typically at one to two orders of magnitude less than upland groundwater concentrations. Sediment lead concentrations were similar between the two zones, although sediment samples from the groundwater discharge zone exhibited lead concentrations at the upper end of the range of the sediment lead concentrations in the low-to-no groundwater discharge zone.

C3.2.5 Groundwater Pathway Assessment for the ARCO Site

Based on an integrated analysis of all discharge mapping and sampling results, two areas of nearshore groundwater discharge were identified at the ARCO site. Other areas offshore of the site were identified as a low-to-no groundwater discharge zone, based on seepage meter measurements, Trident probe temperature measurements, sediment texture, stratigraphic information, and TZW chemistry. These areas are indicated on Figure C3.2-5.

Analysis of the occurrence of COIs in TZW was hampered by the lack of TZW data from one of the groundwater discharge zones and the small number of TZW samples available from the downstream groundwater discharge zone. Although limited, the data suggest

that concentrations of petroleum-related chemicals in TZW are similar in the downstream groundwater discharge zone to those in the low-to-no groundwater discharge zone. Similarly, the concentrations of arsenic do not show any difference in concentrations inside or outside of the groundwater discharge zone, and are similar to levels in upland groundwater. A detailed evaluation of the occurrence of arsenic in TZW at the ARCO site is presented in Section C4.0. Lead concentrations in TZW were orders of magnitude lower than in nearshore upland groundwater.

While it is possible that VOCs, metals, and LPAHs in upland groundwater may be migrating to the transition zone at very low concentrations in the identified discharge zones, the weight of evidence suggests it is more likely that the concentrations of the detected chemicals in TZW are controlled by chemical partitioning to pore water from sediment rather than transport from upland groundwater. This suggests that any migration of chemicals in upland groundwater to the transition zone is not significantly influencing TZW and sediment chemistry at the ARCO site.

C3.3 EXXONMOBIL

The ExxonMobil site is an operational fuel terminal facility located adjacent to the Willamette River at approximately RM 5 (Figure C1.3-1). The site occupies approximately 29 acres and is bounded on the north and south by other petroleum distribution facilities and to the west by St. Helens Road. A set of north/south-trending railroad tracks bisects the site. East of the railroad tracks, there are three aboveground tank farms (the North, Center, and South tank farms) used to store gasoline, diesel, and fuel oils (Figure C3.3-1). A garage, storage building, and a maintenance shop are located in the northern portion of the site, adjacent to the river. A network of distribution lines transports product among the dock, storage tanks, and loading racks. West of the railroad tracks is the Lube Blending Plant, a fuel loading rack, boiler house, and office buildings. An Olympic Pipe Line pumping station and ASTs are also located on the property. This pumping station and associated ASTs are the responsibility of Olympic Pipe Line, not ExxonMobil (SECOR 2002).

A detailed discussion of the ExxonMobil Oil Terminal, including discussion of historical releases, source areas, and remedial measures is presented in the CSM site summary for ExxonMobil (Integral 2007a).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the ExxonMobil site are presented in Table C3.3-1.

C3.3.1 Nature and Extent of Contamination

During historical operations, occasional releases of product from underground pipelines, tanks, and during product transfer operations are known or suspected to have occurred, contaminating surface and subsurface soil and groundwater. Prior to 1970, sludge and residual product from ASTs were released onto the ground during periodic tank cleanings

within the North and Center tank farms. Most of the petroleum hydrocarbons released historically have been found in the vicinity of these tank farms (Kleinfelder 1998). Surface soil was first impacted by the releases, followed by the gradual impact of subsurface soil and groundwater (Kleinfelder 1998). Floating product (LNAPL) was observed at the site prior to 2001. Chemicals of potential concern identified in the Record of Decision (DEQ 1997) included BTEX and PAHs (particularly naphthalene), associated with petroleum releases, and metals (e.g., arsenic, lead, and zinc), some of which may be the result of redox changes in the aquifer caused by high organic carbon levels associated with petroleum releases.

During the 1990s, measurable LNAPL was observed in numerous wells behind the slurry wall and within the North and Center tank farms. By 2001, only trace amounts of LNAPL accumulations were observed at the northern end of the wall and the northern tank farm. LNAPL monitoring and recovery (where possible) are ongoing at the facility. A groundwater plume, consisting of TPH, VOCs, PAHs, SVOCs, and metals commonly associated with gasoline and diesel releases, is present in the shallow aquifer beneath the site. Figure C3.3-2a presents the distribution of LNAPL at the site (based on measurements in November 2004). Figures C3.3-2b–e present the distribution of total BTEX, arsenic, lead, and zinc (expressed as graduated symbols or “bubble plots”) based on recent sampling data available for upland groundwater and TZW. For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater sampling data collected prior to the 2005 implementation of the GWPA. The plume extends from the fuel loading rack on the western portion of the site to the slurry wall along the river to the east, and is generally present beneath the North and Center tank farms. These COIs occur predominantly in the shallow alluvial aquifer (see Section C3.3.3.1), as is illustrated in Figures C3.3-3a and b.

C3.3.2 Completed and Ongoing Remediation Activities

Numerous remedial activities have been completed and/or are ongoing at the site. Cleanup and source control actions to date include the following:

- Installation of extraction wells in northern portion of site in the early to mid-1970s.
- Installation of 14 large-diameter extraction wells (“eductor wells”) adjacent to river to prevent free product movement to the river (1977). Exxon ceased operation of these wells in early 1990s.
- A slurry wall constructed to act as barrier to the movement of shallow groundwater and free petroleum product in the early 1980s.
- Recovery of free petroleum product from the shallow aquifer (1970s–ongoing).
- Installation and operation of air sparging and soil vapor extraction (SVE) systems to reduce contaminants in soil and groundwater (2000–ongoing).

- SVE/air sparging expansion is planned for the area where contaminated groundwater is discharging to the river between the slurry wall and the ARCO site.

According to DEQ's September 2010 Milestone Report (DEQ 2010), additional source control measures were to be implemented in Q4 2010 at the ExxonMobil site to address a "hydraulic gap" identified near the downstream end of the site.

C3.3.3 Evaluation of Groundwater Discharge

The following presents an evaluation of multiple lines of evidence to interpret the extent of probable groundwater discharge at the ExxonMobil site.

C3.3.3.1 Hydrogeology

Results from the subsurface borings indicate that the general site stratigraphy from the ground surface downward consists of the following (Kleinfelder 1998; DEQ 1997):

- Fine to medium sand (fill) – (shallow alluvial aquifer)
- Silty-clay – (aquitar)
- Silty, fine sand – (deep alluvial aquifer)
- CRBG.

The general site stratigraphy is depicted in the cross section presented in Figures 3.3-3a and b. Basalt is typically encountered at depths of 20 ft bgs or less along the western edge of the facility and at depths of about 60 ft bgs adjacent to the river. Across the site, silty, fine sand overlies the basalt. Beneath the eastern portion of the site (from the railroad tracks to the river), a silty-clay aquitar unit overlies the silty, fine sand. The aquitar does not extend beneath the western portion of the site. The top of the silty-clay aquitar is either at or just below (2–3 ft) ground surface along the western edge of the site adjacent to the railroad tracks, and dips to depths of 30 ft bgs adjacent to the river. This unit appears contiguous based on the current monitoring well network and extensive borings conducted for the design of a slurry wall installed in the early 1980s. The top of the aquitar unit is partially exposed along the riverbank during periods of low river stage. This aquitar unit separates the shallow and deeper aquifers beneath the eastern half of the facility.

The aquitar is overlain to ground surface in the eastern half of the facility by fine to medium sand, which comprises the upper (shallow) aquifer. This material appears to be dredge spoils placed on top of the aquitar during past river-dredging operations. In the early 1980s, a slurry wall was installed that extends from the southern property line to the southern end of the North Tank Farm (Figure C3.3-1). The wall is installed as close to the river as practicable and is keyed into the aquitar beneath the site (Integral and Kleinfelder 2003). A seawall extends from the downstream property line to the upstream

area of the dock (adjacent to the downstream end of the Center Tank Farm), but is not keyed into the aquitard.

Groundwater flow in the shallow zone follows a gradient of ~ 0.035 ft/ft to the northeast (towards the river); however, the flow direction is locally deflected by the slurry wall to the north or south ends of the property. The shallow water-bearing zone has a hydraulic conductivity of ~ 4 ft/day (Integral and Kleinfelder 2002). The deep water-bearing zone is less characterized, and there are no current monitoring wells completed within this unit.

C3.3.3.2 Groundwater Discharge Mapping Field Investigations

In 2005, discharge mapping was performed at the ExxonMobil site, in accordance with the Discharge Mapping FSP (Integral 2005c), to help focus the subsequent TZW sampling effort. The following summarizes the results of the discharge mapping field investigations. Detailed results of the discharge mapping are presented in SAP Addendum 1 (Integral 2006a).

In all, 42 in-river measurements were made with the Trident probe (Figure C3.3-4). Additionally, ultrasonic seepage meters were installed for 24-hr periods at six of the Trident locations offshore of the ExxonMobil site. This groundwater discharge mapping effort primarily focused on the area at the northern end of the site where the slurry wall is absent. Additional discharge mapping data were collected offshore of an abandoned former wooden sewer line on the south side of the dock area, as well as at several locations offshore of the slurry wall, to evaluate whether a potential pathway for groundwater COI migration to the river may exist in the form of a remnant plume.

C3.3.3.2.1 Surface Sediment Texture

Figure C3.3-4 presents the interpreted distribution of offshore sediment textures based on the Trident observations and from textures recorded in grab samples during the discharge mapping and past sediment sampling events. Several zones of surficial sand are present along portions of the site shoreline. Surface sediment texture grades to a fairly continuous zone of silty-sand to sandy-silt farther offshore. At the most offshore mapping locations, sediments tend to be silt. The distribution of surface sediment textures is generally consistent with the projection of the upland stratigraphy into the river (Figures C3.3-3a and b).

C3.3.3.2.2 Trident Probe Temperature Mapping

The ExxonMobil site displayed the same general patterns as those observed during the GWPA Pilot Study (Integral 2005d), with the nearshore sands typically showing smaller temperature differences and the offshore silts showing greater differences. It is hypothesized that the smaller temperature differences observed in sand are the result of greater mixing between groundwater and surface water in coarser- versus finer-grained sediments.

Exceptions to this general pattern were observed at locations EM3-A, EM4-A, and EM8-A. These exceptions may indicate areas of higher groundwater flux to the river and a resulting suppression of the effects of mixing with surface water on TZW temperature and conductivity. This suppression would result in greater temperature differences than those observed in other coarse-grained sediments where groundwater discharge to the river is less significant. The anomaly in the Trident temperature data at EM8-A suggests a potential area of higher groundwater discharge in the nearshore area near the southern end of the dock structure, where the former wooden sewer pipe was located.

C3.3.3.2.3 Seepage Rate Measurements

Seepage meters were installed at six of the Trident locations offshore of the ExxonMobil site: EM1-A, EM1-D, EM3-A, EM3-D, EM5-A, and EM-11A. These seepage meter locations are designated EMSEEP 1A, EMSEEP 1D, EMSEEP 3A, EMSEEP 3D, EMSEEP 5A, and EMSEEP 11A. Results of the seepage meter measurements are presented in Figure C3.3-4. Average specific discharge rates of 4.0 to 9.8 cm/day were measured at locations in the nearshore sand and sand/silt, whereas average specific discharge rates of -18.9 to 1.2 cm/day were measured in the siltier materials farther offshore and at location EM-11A (which is located offshore of the slurry wall).

C3.3.3.3 Interpretation of Groundwater Discharge Zones

Trident temperature, sediment texture, and seepage meter results were consistent with the understanding of the site hydrogeology, which suggests that the surficial water-bearing unit intersects the river near the site shoreline, north of the slurry wall. The combined lines of evidence suggest that the shallow groundwater and associated COI discharge are likely occurring primarily through the nearshore sandy zones.

Figure C3.3-5 presents the interpreted zones of groundwater discharge. The sandy nearshore groundwater discharge zone area includes the locations of the positive average seepage meter measurements that ranged from 4.0 to 9.8 cm/day. This area also includes the sandy sediment area around the former wooden sewer outfall where anomalous Trident temperature readings indicated likely groundwater discharge. The lower flow rate groundwater discharge zone, located immediately offshore of the nearshore zone, was designated based on the low-but-measurable average seepage meter reading of 1.2 cm/day at EMSEEP 1D. This zone was drawn largely to correspond to the mixed sand and silt surface sediment texture, which generally extends to the outer edge of the dock structures. It is expected that this zone may include areas of low-to-no groundwater discharge.

Finally, the region shown with tan shading on Figure C3.3-5 is mapped as a low-to-no groundwater discharge zone. This zone is defined beyond the dock area by stratigraphic cross-section projection, surface sediment texture, and Trident temperature trends—all of which are consistent with an absence of groundwater discharge to this zone. South of the dock area, offshore of the slurry wall, the low-to-no flow zone extends to the shoreline because no groundwater discharge is expected to bypass the slurry wall. EMSEEP 11A showed no positive discharge, supporting this interpretation.

C3.3.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

A total of 13 TZW samples were collected from 10 locations, shown on Figure C3.3-1. Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the ExxonMobil site. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from a target depth of at 120 to 150 cm at three of the locations. The rationale for selection of the sampling locations was as follows:

- Samples were collected from six locations (EM1-A, EM2-A, EM3-A, EM4-A, EM5-A, and EM6-B) in the nearshore sand and sand/silt sediments along the northern shoreline of the site, where the potential for groundwater COI discharge is likely the greatest due to the absence of the slurry wall in this area. Paired samples at depths of 150 and 120 cm were collected EM1-A and EM3-A, respectively.
- Samples were collected from two locations (EM8-A and R2-EM-1) that are located farther to the south along the site shoreline. At location EM8-A, an anomalously high Trident temperature difference was recorded, suggesting that preferential groundwater discharge may be occurring in this area, which is coincident with the outfall location of an abandoned former sewer line. Location R2-EM-1 was sampled to evaluate the potential for COI discharge associated with a remnant plume that has been speculated to exist offshore of the slurry wall.
- Samples were collected at two locations (EM2-C and EM4-C) farther offshore at the northern end of the site. This sampling was performed by agreement with USEPA and its partners (USEPA 2005a, pers. comm.) to provide information farther offshore for reference and to support data interpretation. A paired sample at a depth of 150 cm was collected at EM4-C.

C3.3.4.1 Major Ion Chemistry

Figure C3.3-6 presents the major ion composition for TZW and upland groundwater at the ExxonMobil site, and compares it to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are linearly scaled from 0 to 2,200 mg/L. In addition, Table C3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the ExxonMobil site TZW samples was typically ± 10 percent or less, with most samples being anion deficient—likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis.

Groundwater, TZW, and river water at the site are all predominantly calcium-carbonate waters; however, the river water shows a greater influence of sodium and chloride than is shown by the TZW and upland groundwater samples. TZW major ion composition is not significantly different in samples collected from the interpreted groundwater discharge zone than those collected from the zone where low-to-no groundwater discharge is estimated to be taking place. These data suggest that the TZW major ion composition is

influenced by geochemical interactions within the sediment pore space (e.g., mineral dissolution and precipitation, microbial processes) and that these processes are similar to those acting in the upland aquifer to establish the groundwater major ion composition.

C3.3.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figure C3.3-5 shows the locations of the TZW sample stations and sediment sample stations relative to the three groundwater discharge zones identified at the site. Figures C3.3-7a–d compare the range of concentrations for select COIs in groundwater in nearshore wells to the range of COI concentrations in TZW and sediment measured across the two groundwater discharge zones relative to the low-to-no groundwater discharge zone. These data are also presented in Table C3.3-1. The following summarizes the findings of this analysis:

- **BTEX (Figure C3.3-7a)** – The majority of BTEX results in TZW collected at the ExxonMobil site were below detection. Where detected, concentrations of BTEX in TZW were similar in the TZW samples collected from the two groundwater discharge zones and the low-to-no groundwater discharge zone. Further, the detected TZW concentrations in all three of these zones were 2 to 3 orders of magnitude less than the concentrations in upland groundwater. BTEX was only detected in one sediment sample across both of the groundwater discharge zones, at a concentration that was slightly higher than the upper end of the range of detected BTEX concentrations in sediment samples from the low-to-no groundwater discharge zone.
- **Arsenic (Figure C3.3-7b)** – Dissolved concentrations of arsenic were comparable in upland groundwater to TZW samples from both groundwater discharge zones. The TZW sample from the low-to-no groundwater zone exhibited a similar concentration to the TZW samples from the groundwater discharge zones; however, the data are too limited to make a definitive conclusion of the relative concentrations in these zones. In general, the arsenic concentrations in TZW and upland groundwater at the ExxonMobil site were slightly elevated compared to the range of arsenic concentrations measured in background groundwater wells (see Section C4.0). Sediment concentrations of arsenic were not substantially different in the groundwater discharge zones from the low-to-no groundwater discharge zone.
- **Lead (Figure C3.3-7c)** – The ranges of dissolved lead concentrations were similar in upland groundwater and in TZW samples from both groundwater discharge zones. Lead was not detected in the sample from the low-to-no groundwater discharge zone. Sediment lead concentrations were similar in the low-to-no groundwater discharge zone and the lower flow rate groundwater discharge zone, and were somewhat lower in the other groundwater discharge zone.
- **Zinc (Figure C3.3-7d)** – The ranges of dissolved zinc concentrations were similar in TZW samples from both groundwater discharge zones offshore of the

ExxonMobil site. The TZW sample from the low-to-no groundwater zone exhibited a zinc concentration at the lower end of the range of concentration measured in the TZW samples from the groundwater discharge zones; however, the data are too limited to make a definitive conclusion of the relative concentrations in these zones. TZW zinc concentrations tended to be at the lower end of the range of concentration observed in upland groundwater. Sediment zinc concentrations were not substantially different in the groundwater discharge zones and the low-to-no groundwater discharge zone.

C3.3.5 Groundwater Pathway Assessment for the ExxonMobil Site

Based on an integrated analysis of all discharge mapping and sampling results, two nearshore groundwater discharge areas were identified at the ExxonMobil site. Although TZW and sediment samples from the ExxonMobil site indicate the presence of petroleum-related chemicals, concentrations of total BTEX were substantially lower in TZW than in upland groundwater monitoring wells. Concentrations of arsenic and zinc do not show substantial differences in concentrations inside or outside of the groundwater discharge areas, and were generally consistent with levels measured in upland groundwater. Lead was detected in filtered TZW samples from the two groundwater discharge zones, but was not detected in the single filtered sample from the low-to-no groundwater discharge zone. In unfiltered TZW samples, lead was detected in all three zones and at higher concentrations than in the filtered samples, indicating the influence of the particulate fraction on unfiltered (total) lead concentrations. As with arsenic and zinc, detected concentrations of lead in TZW were generally consistent with the range of concentrations in upland groundwater. Overall, the TZW data set, while limited, suggests that BTEX and metals in upland groundwater at the ExxonMobil site may have been transported to the TZW via groundwater flow prior to the implementation of upland groundwater source control measures. It is also plausible that the chemicals detected in TZW samples collected during the RI at the ExxonMobil site reflect chemical partitioning from sediment to pore water rather than transport from upland groundwater.

C3.4 GASCO

The Gasco site is located on the western shore of the Willamette River at approximately RM 6 (Figure C1.3-1). The 44.5-acre site is bordered by the Willamette River to the northeast, a Burlington Northern Santa Fe Railroad Company (BNSF) railroad right-of-way to the southwest, Siltronic Corporation to the southeast, and the U.S. Army Corps of Engineers Moorings Station (U.S. Moorings) to the northwest (Figure C3.4-1). U.S. Highway 30 (NW St. Helens Road), a former rock quarry, an automobile impound yard, and the Tualatin Mountains lie beyond the BNSF right-of-way to the southwest.

Currently, the central portion of the site is used by NW Natural as a liquefied natural gas (LNG) storage and distribution facility. The southern portion of the site is leased by Koppers Industries, Inc. (KI) for use as a coal tar pitch distribution facility. The northern portion of the site is leased by Fuel and Marine Marketing, Inc. (FAMM) for use as a bulk fuel storage and distribution terminal. Overwater activities include transfer of bulk

petroleum (by FAMM) and heated liquid coal tar pitch (by KI) from barges to onsite bulk storage facilities. Potential sources of contamination at the Gasco site include process or operational areas and by-product and residue placement areas.

A detailed discussion of the Gasco site, including discussion of historical releases, source areas, and remedial measures is presented in the CSM site summary for Gasco (Integral 2007a).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the Gasco site are presented in Table C3.4-1.

C3.4.1 Nature and Extent of Groundwater Contamination

Tar and oil have been identified at portions of the site and the adjacent Siltronic site. DNAPL has been identified at thicknesses up to 10 ft within three wells in the surficial fill, all located at the central portion of the site approximately 350 to 750 ft upland from the Willamette River shoreline (Integral and GSI 2004). NAPL has also been observed in the former tar pond effluent discharge areas, as well as in an area to the northeast of these locations (Figure C3.4-2a). Dissolved groundwater plumes consisting of constituents associated with oil tar (PAHs), as well as oil tar distillates (e.g., BTEX) and elevated concentrations of dissolved metals, are present in groundwater beneath portions of the site. Concentrations of total BTEX, naphthalene, and total cyanide in upland groundwater and TZW are presented in Figures C3.4-2b–d. For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater sampling data collected prior to the 2005 implementation of the GWPA. The concentrations for the individual chemicals are expressed on the figures as graduated symbols (or bubble plots).

Figures C3.4-3a–f present the concentrations of total BTEX, naphthalene, and total cyanide in groundwater samples projected on representative stratigraphic cross sections located parallel and perpendicular to the shoreline. These figures illustrate that elevated concentrations of COIs are present in groundwater throughout much of the thickness of the fill and alluvium underlying the site. At the shoreline, elevated concentrations of these chemicals extend from the western end of the Siltronic site across the eastern approximate half of the Gasco site.

C3.4.2 Completed and Ongoing Remediation Activities

Pilot-scale DNAPL extraction activities were conducted at the site in 1999 to evaluate the recoverability of DNAPL from applicable wells. Results of pilot-scale testing indicated DNAPL recovery from the MW-6-32 well location was feasible, and recovery was implemented in 2000.

Shallow groundwater that seeps into the LNG containment basin (Figure C3.4-1) is removed and treated in an onsite carbon adsorption system prior to discharge to the Willamette River via a permitted wastewater treatment system. Although the objective of

this recovery and treatment system is not source-control-based or remediation-based, groundwater is removed and treated from the central portion of the site where some of the greatest COI concentrations within the surficial fill water-bearing zone are located (Integral and GSI 2004).

In 2005, NW Natural performed a removal action at the Gasco site to remove a “tar body” from the nearshore sediment adjacent to the site. An engineered pilot cap was placed as a barrier over the tar body removal area. Since 2007, Gasco and DEQ have been conducting engineering studies to support the selection and design of source control measures to address migration of dissolved-phase groundwater contamination and DNAPL concerns. As of the September 2010 DEQ Milestone Report (DEQ 2010), DEQ had conditionally approved the “Segment 2” design to address dissolved-phase contamination using hydraulic containment. Final source control cleanup decisions for “Segment 1”, which includes DNAPL in the former tar pond area, are pending the outcome of a formal dispute resolution process initiated by Gasco regarding Segment 1.

Pending future implementation of a site-wide remedy, long-term monitoring of the removal action area has been conducted since 2006 to 1) monitor the performance of the remedy with respect to the removal action objectives (RAOs), and 2) evaluate the performance of the engineered pilot cap as a method to minimize chemical movement from underlying sediments.

C3.4.3 Evaluation of Groundwater Discharge

The following presents an assessment of groundwater discharge associated with the Gasco site based on multiple lines of evidence.

C3.4.3.1 Site Hydrogeology

The site stratigraphy is depicted in the two generalized cross sections presented in Figures C3.4-3a–f. The locations of these cross sections are shown on Figure C3.4-1. The general site stratigraphy from the ground surface downward consists of the following units (Integral and GSI 2004):

- **Surficial Fill** – The thickness of the surficial fill ranges from approximately 2 ft along the western portion of the site to a maximum of approximately 30 ft in the northern and eastern portions of the site, near the Willamette River. Much of the fill at the site, especially in the northwestern and central areas, consists of poorly graded sands and silty sands that are likely river-dredge material. Other areas of the site contain lampblack and/or pencil pitch material, solidified tars, oil, quarry reject rock, and building debris, which were either historically discharged to low areas of the site and/or were incorporated into the fill when these areas were brought to current grade (Integral and GSI 2004).
- **Alluvium** – Underlying the surficial fill at the site are Quaternary-age alluvial deposits, composed of unconsolidated sands and silts, which range in thickness from approximately 30 ft near St. Helens Road to an estimated thickness of

approximately 200 ft adjacent to the Willamette River near the northern corner of the adjacent Siltronic site. Borings installed at the site encountered a laterally extensive fine-grained silt unit, with minor clay content, at the uppermost portion of the undifferentiated alluvial deposits (Integral and GSI 2004). Fine- to medium-grained sands, silty sands, sandy silts, and relatively thin interbedded silts were encountered below the silt unit within the undifferentiated alluvial deposits. A thin layer consisting of medium- to coarse-grained sandy gravel has been observed at the base of the alluvial deposits at the Gasco site and the adjacent Siltronic site. The thickness of the upper silt unit is greatest in the central-southeast portion of the site, where thicknesses of up to 43 ft have been identified. The silt unit appears to thin in all directions from this area of the site, apart from to the south-southeast, where thicknesses of 56 to 69 ft were identified extending across the entirety of the central portion of the adjacent Siltronic property. The silt appears either to diminish to within 1 to 3 ft thick, is locally absent, and/or transitions to a silty sand in the vicinity of the Willamette River.

- **Columbia River Basalt** – The CRBG underlies the alluvial deposits. From the Tualatin Mountain outcropping, the basalt surface dips steeply to the northeast, with the top of the basalt lying at an elevation near mean sea level (a depth of approximately 36 ft bgs) in the southern corner of the site to depths of 215 ft bgs near the southeastern corner of the Gasco site.

As described by Anchor (2008), numerous borings were completed offshore of the site during NW Natural's 2006–2007 offshore investigations, with several drilled through the full thickness of the alluvium to the underlying basalt. The Anchor (2008) report includes additional cross sections depicting the nearshore stratigraphy. The primary difference between the offshore and the upland geology is the absence of the surficial fill layer, which is present across much of the upland site area. The shoreline/offshore alluvium is consistent with that observed beneath the upland site, consisting primarily of sand to silty sand, interbedded with silt to sandy silt.

Groundwater occurs in three principal hydrologic zones beneath the site, which from top to bottom include the following: 1) the unconfined surficial fill water-bearing zone (WBZ); 2) the semi-confined alluvial WBZ; and 3) the confined bedrock aquifers in the CRBG. Water-bearing zones within the CRBG are not monitored at the site. Figure C3.4-1 shows the potentiometric surface for the shallow fill WBZ. Groundwater flow in the shallow fill WBZ is generally toward the river, although locally, groundwater flow patterns are influenced by pumping from the LNG containment basin.

A downward vertical hydraulic gradient is typical between the fill WBZ and the underlying alluvial WBZ (Hahn and Associates 1998). Consequently, groundwater in the fill WBZ has the potential to migrate to the alluvial WBZ at portions of the site. Groundwater flow in the alluvial WBZ is also toward the river, with the majority of the flow likely occurring in more permeable sands that predominate in the lower portion of the alluvial deposit (Figure C3.4-3a–f). Vertical hydraulic gradients based on the potentiometric surface measured in wells completed at varying depths in the alluvial

deposit typically fluctuate from between -0.0005 to -0.005 ft/ft (upward) and between 0.002 and 0.008 ft/ft (downward), with the downward gradient predominating in the upper alluvial deposit, and the upward gradient predominating in the lower alluvial deposit.

C3.4.3.2 Groundwater Discharge Mapping Field Investigations

The 2005 groundwater discharge mapping was performed at the Gasco site in accordance with the Discharge Mapping FSP (Integral 2005c) to help focus the subsequent TZW sampling effort. In all, 43 in-river measurements were made with the Trident probe (Figure C3.4-4). The mapping locations focused on the nearshore area across the length of the site to better understand the extent of the silt layer in this area and evaluate its effect on shallow groundwater discharge. Of particular interest was the central to southeastern portion of the site, where groundwater COIs originating from both the Gasco and Siltronic sites are observed at relatively high concentrations in upland groundwater samples. Ultrasonic seepage meters were installed for 24-hr periods at seven of the Trident locations offshore of the Gasco site.

A large portion of the southern end of the site could not be evaluated during the 2005 investigation due to access limitations during the tar body removal action. NW Natural's 2006–2007 offshore investigation (Anchor 2008) spanned the entire length of the shoreline adjacent to, as well as somewhat upstream and downstream of, the site (Figure C3.4-5a). This investigation involved the following elements:

- Completion of borings and collection of TZW and groundwater samples along four offshore transects parallel to the riverbank and spanning from upstream of the site (adjacent to the southern end of the Siltronic site) to downstream of the site. A total of 32 borings were completed and 211 TZW/groundwater samples collected.
- Ultrasonic seepage meters were installed at seven locations for a five-day period.
- Mini-piezometers were installed at three offshore locations and 30 TZW samples were collected to evaluate if there is a correlation between river stage and TZW concentration.
- Surface water grab samples were collected at 20 locations from RM 5.9 to 6.7. In October 2007 at each location, near-surface, mid-depth, and near-bottom samples were collected in low-flow conditions, during three tidal periods: ebb, slack high, and slack low. A total of 180 surface water samples were tested for field parameters, cyanide, total and dissolved iron, sulfide, dissolved organic carbon, and total organic carbon. Surface water samples collected during this investigation were not tested for VOCs or SVOCs.

Key findings of this investigation, as they relate to the GWPA, are described herein. A complete description of the findings of NW Natural's 2007–2008 offshore investigation can be found in Anchor (2008).

C3.4.3.2.1 Surface Sediment Texture

Figure C3.4-4 presents the distribution of offshore surface sediment textures based on Trident mapping and direct observations during the LWG Round 2 surface sediment sampling, NW Natural's 2007–2008 offshore investigation, and other sediment sampling events. Sand extends offshore from the riverbank to about the 0-ft-mean sea level (msl) bathymetric contour in the central and southern portion of the site shoreline. Surficial sediments consist of silts and sandy silts in the area beyond this sand zone and in shoreline sediments adjacent to the northern portion of the site. The shoreline sand zone is absent in the vicinity of the small embayment associated with the Siltronic outfall, but it reoccurs farther north, offshore of the Siltronic site.

C3.4.3.2.2 Trident Probe Temperature Mapping

The results of the 2005 Trident temperature mapping are summarized in Figure C3.4-4. In general, the Gasco site displayed the same general patterns as those observed during the GWPA Pilot Study (Integral 2005d) and at other sites evaluated during the 2005 discharge mapping investigation, with the nearshore sands generally showing smaller temperature and conductivity differences and the offshore silts showing greater differences. Exceptions to this general pattern were observed at transects GSC4 through GSC7, with many of the nearshore sand locations (e.g., GSC5-B) displaying greater temperature differences than other nearby transect locations in similar sediment types. These results may indicate areas of higher groundwater flux and a resulting suppression in the effects of mixing with surface water on TZW temperature and conductivity.

C3.4.3.2.3 Seepage Flux Measurement

Seepage meters were installed at eight of the Trident probe locations offshore of the Gasco site during the 2005 investigation: GSC2-A, GSC3-A, GSC4-A, GSC4-C, GSC4-E, GSC7-B, GSC7-D, and GSC7-F. These seepage meter locations are designated as GCSEEP 2A, GCSEEP 3A, GCSEEP 4A, GCSEEP 4C, GCSEEP 4E, GCSEEP 7B, GCSEEP 7D, and GCSEEP 7F (Figure C3.4-4). Due to significant sediment offgassing during the seepage meter measurements, only limited data could be collected from location GSC7-B. Further, no data could be collected at GCSEEP 7D due to an equipment failure (this meter is not shown on Figure C3.4-4). The average seepage flux measurements, presented in Figure C3.4-4, ranged from -2.1 to 5.7 cm/day. The discharge rates measured at the majority of the locations were low (<1 cm/day). The greatest discharge rate was recorded at GCSEEP 7B, where average and maximum specific discharge rates of 5.7 and 8.7 cm/day were recorded, respectively. A continuous positive flux was also recorded at location GCSEEP 3A, where average and maximum specific discharge rates of 3.7 and 6.0 cm/day were recorded, respectively.

Seven seepage meters were also deployed at the site as part of the 2007-2008 offshore investigation (Figure C3.4-4). Seepage flux data were successfully collected at six out of seven target stations. No data were recorded at station GS-B5, as the data logger was inadvertently not activated during installation. With the exception of GS-B7 (average discharge rate of -0.05 cm/day), the mean groundwater flow rate at all stations indicated low level groundwater discharge at rates ranging from 0.05 to 1.47 cm/day. The mean

groundwater discharge rate in the pilot cap at GS-PC1B (1.03 cm/day) was comparable to rates observed at other stations.

C3.4.3.3 Offshore Groundwater Concentrations of COIs

A primary focus of the 2007-2008 offshore investigation was the quantification of COI concentrations in groundwater collected offshore of the site. Results of this investigation are presented in detail in Anchor (2008) and focus on describing the nature and extent of manufactured gas plant (MGP)-related COIs, including free cyanide, total cyanide, benzene, toluene, naphthalene, and benzo(a)pyrene (BaP). These analytes represent a wide range of subsurface fate and transport properties, and their distribution is generally representative of the MGP-related COIs at the site. The Anchor (2008) report includes a detailed description of each of these COIs in groundwater and TZW along numerous cross sections oriented both parallel and perpendicular to the site. Figures C3.4-5b–d present 3-D visualizations of the offshore distribution of each of these COIs prepared by Anchor (2008). As discussed above, Anchor (2008) collected 60 near-bottom surface water samples from 20 locations, under three separate tidal regimes. The near-bottom surface water samples were analyzed for cyanide (free, total, and amenable), but were not analyzed for VOCs or SVOCs. TZW concentrations of total BTEX, naphthalene, and total cyanide are shown on the bubble plots in Figures 3.4-2b–d.

As described in Anchor (2008), a summary of the findings of Gasco's offshore groundwater investigation include the following:

- The depth, lateral extent, and concentration of COIs in offshore groundwater varies significantly for each COI. The complex distribution of COIs is largely a function of the long history of manufacturing at the site, variations in operational practices over time, and the types of products that were manufactured.
- Free cyanide has been detected in a very small percentage of the groundwater samples, and at trace concentrations where detected. This is significant because the free cyanide compound is considered the toxic form of cyanide. The detected concentrations were generally below 10 µg/L. Free cyanide was not detected in any near-bottom surface water samples.
- Total cyanide is present in groundwater in all offshore transects at generally all depths sampled. Total cyanide is very soluble, chemically stable, and does not adsorb significantly to the sediment matrix. Therefore, total cyanide is one of the most widely distributed of the MGP-related COIs.
- Total cyanide was detected in only three of 60 near-bottom surface water samples collected from 20 sampling locations under three different tidal regimes (low tide, high tide, and falling tide). One of these (GSW-01) was a downstream reference sample collected under high tide conditions. The other two detections of total cyanide were at near-bottom sample locations GSW-09 and GSW-14 (Figure C3.4-5a), both collected under falling tide conditions. In the sample collected from GSW-09, total cyanide was detected at a concentration of 10 µg/L in the

total (unfiltered) fraction and at a concentration of 140 µg/L in the dissolved (filtered) fraction. Anchor (2008) noted the apparent anomaly between in the total and dissolved fraction in this sample (which also occurred for amenable cyanide), but identified “no indication of any systematic sampling artifact created by the sample collection or filtering process.” In the sample collected from GSW-14, total cyanide was detected at a concentration of 110 µg/L in the total fraction and was undetected, at a detection limit of 3 µg/L, in the dissolved fraction.

- The distribution of total cyanide in offshore groundwater appears to reflect two general sources. The first source is groundwater transport from two upland source areas, as well as the upland former spent oxide storage pile area on the north end of the shoreline and the former upland effluent settling pond area. The second source is direct discharge of liquid wastes to areas that appear to have drained to the river on the south end of the site, and direct placement of spent oxides along the shoreline on the north end of the site.
- Benzene, toluene, and naphthalene are also widely distributed, but their plume patterns are variable, reflective of historical direct discharge or overflow of oily effluent to the river and groundwater transport from upland sources. Benzene, toluene, and crude naphthalene were manufactured as separate products, which may have influenced their offshore distribution in groundwater.
- Consistent with a much higher tendency of BaP to adsorb to organic carbon, its distribution in groundwater is quite limited compared to naphthalene (another PAH), which is much more mobile in groundwater. The presence of elevated BaP concentrations in offshore groundwater is primarily associated with the occurrence of NAPL in shallow sediments. Although trace concentrations of BaP are detected in some of the deeper groundwater samples, these are likely associated with the suspended solids in the groundwater grab samples obtained in this investigation.

C3.4.3.4 Interpretation of Groundwater Discharge Zones

Figure C3.4-6 presents an interpretation of groundwater discharge zones at the Gasco site based on the lines of evidence described above. Trident temperature, sediment texture, and seepage meter results are consistent with the understanding of the site hydrogeology and subsurface stratigraphy. In nearshore areas that roughly correspond with the projection of the silts and interbedded sands of the nearshore shallow alluvium into the river, the discharge mapping results suggest a nearshore zone of variable groundwater discharge, with variability likely attributable to the variable presence and thickness of the subsurface silt layers. This variability is reflected in seepage meter results from nearshore areas; net positive average discharge measurements of 3.67 and 5.67 cm/day were recorded at GCSEEP-3A and GCSEEP-7B, respectively; but no significant discharge was observed at GCSEEP-2A and GCSEEP-4A (average seepage rates of 0.24 and -0.07 cm/day, respectively). Trident temperature differences shown on Figure C3.4-4 show some anomalously high measurements in nearshore areas (e.g., GSC-4A, GSC-5B, GSC-6A); however, the seepage meter placed at Trident location GSC-4A (GCSEEP-4A) indicated an average negative seepage flux. As such, the temperature

anomalies are not definitively indicative of areas of preferential groundwater discharge to the nearshore area. Given the variable presence and thickness of silt in the shallow alluvium, variability in shallow groundwater conditions in the nearshore area is expected.

Low rates of discharge were observed at intermediate water depths between this nearshore area and the toe of the slope that defines the navigation channel. In-water discharge mapping results (e.g., seepage meter results for sediment texture) are consistent with the predominantly silty (with some sand) texture of the alluvial deposits at this depth (Figure C3.4-4). Temperature mapping showed no significant indication of preferential groundwater discharge in this zone (Figure C3.4-4). Seepage meters located within this zone recorded average flux rates ranging from -2.13 cm/day (GCSEEP-4C) to 1.0 cm/day (GCSEEP-4E).

Farther offshore (i.e., at or near the toe of the slope that defines the navigation channel), stratigraphic information suggests the possible presence of a deeper groundwater discharge zone. Average seepage flux measurements at locations GCSEEP-7F, GS-C5, GS-C7, and GS-D5 ranged from 0.33 to 1.47 cm/day. A deeper discharge area at this depth would be consistent with the interpretation for the adjacent Siltronic site (Section C3.5.3.4). This area of potential discharge, however, is not strongly indicated by temperature differences.

The findings of NW Natural's offshore groundwater COI investigation are consistent with the site stratigraphy and the findings of the Trident temperature mapping, sediment texture, and seepage meter results. As illustrated in Figures C3.4-2b-d and 3.4-5b-d, the distribution of COIs in offshore groundwater suggests that groundwater discharge occurs predominantly to the nearshore sediments, but also to a variable extent to sediments farther offshore. Concentrations observed in groundwater and TZW in the farthest offshore locations are considerably lower than those observed in the nearshore samples, suggesting that the majority of groundwater plume discharge occurs in the nearshore area.

C3.4.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

A total of eight TZW samples were collected from six locations during the 2005 TZW sampling event (Figure C3.4-6).¹⁵ Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the Gasco site. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from a depth of 150 cm at two of the locations. The rationale for selection of the sampling locations was as follows:

- Samples were collected from two locations within the nearshore zone in the southern (upstream) portion of the site (GSC7-B and GSC8-A). These locations

¹⁵ Access limitations during the in-water removal of the tar body at Gasco during summer and fall of 2005 prevented the collection of seven TZW samples from five locations as originally specified in Addendum 1 of the FSP: GSC-04A (30 cm and 90 cm), GSC-05-A (30 cm and 90 cm), GSC-05-B (30 cm), GSC-06-A (30 cm), and GSC-06-D (30 cm).

are immediately offshore of the area where COI concentrations are elevated in upland shallow groundwater, focusing on areas of predominantly sandy surface sediments, although underlying layers of silt occur in some locations within these areas. Additional sampling in the nearshore area in the central portion of the site could not be performed due to access limitations.

- Samples were collected from two locations (GSC1-B and GSC2-A) in the nearshore area at the northern (downstream) portion of the site to evaluate the potential discharge of upland groundwater COIs in this portion of the site.
- Samples were collected from two locations (GSC7-D and GSC8-D) in the silty area offshore from the nearshore surface sand area where groundwater discharge conditions are indeterminant, but may be lower than in some nearshore areas due to the increased presence of sand in surface deposits and, across some portions of the shoreline, in subsurface alluvium within this elevation range. Paired samples at a depth of 150 cm were collected at both of these locations.

In addition, TZW samples were collected at each location along the four offshore transects (32 locations total) during Gasco's 2007-2008 offshore investigation. These samples were collected using a mini-piezometer with a screen mid-point at a depth of 1.5 ft bml.

C3.4.4.1 Major Ion Chemistry

Figure C3.4-7 presents the major ion composition for TZW at the Gasco site, and compares it to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are linearly scaled from 0 to 2,200 mg/L. In addition, Table 3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the Gasco site TZW samples was typically -20 percent or less; although one sample had a charge imbalance of -36 percent. All of the samples were anion deficient, likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis.

TZW and river water at the Gasco site are both predominantly calcium-carbonate waters; however, the river water shows a greater influence of sodium and chloride than is shown by the TZW and upland groundwater samples. TZW major ion composition is not significantly different in samples collected from the interpreted zones where groundwater discharge may be occurring than from the samples collected from the zone where low-to-no groundwater discharge is taking place. These data suggest that the TZW major ion composition is primarily influenced by geochemical interactions within the sediment pore space (e.g., mineral dissolution and precipitation, microbial processes), and that groundwater discharge does not significantly alter the TZW major ion composition.

C3.4.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figures C3.4-8a–f present the range in concentration of benzene, toluene, naphthalene, BaP, and free and total cyanide observed in TZW and sediment samples collected from

the groundwater discharge zones and the low-to-no groundwater discharge zone identified at the Gasco site. These data are also presented in Table C3.4-1. The TZW concentrations are also compared to the range of concentrations observed in nearshore, upland groundwater, and “in-river” groundwater samples (i.e., groundwater samples collected from the aquifer below the transition zone).

- **Benzene (Figure C3.4-8a)** – For both TZW and sediment, benzene generally exhibited comparable ranges of concentrations across the various groundwater discharge zones (including the low-to-no groundwater discharge zone). The data tend to suggest that benzene concentrations in both TZW and sediments may be somewhat lower in the offshore groundwater discharge zone than in the nearshore and low-to-no groundwater discharge zones. The majority of the TZW benzene concentrations are toward the lower end of the range of concentration observed in the in-river and nearshore, upland groundwater samples—particularly in the offshore discharge zone. TZW concentrations of benzene in a few samples from the low-to-no groundwater discharge zone and the variable nearshore groundwater discharge zone were at or near the high end of the concentration range observed in the in-river groundwater samples.
- **Toluene, Benzo(a)pyrene, Naphthalene, Free Cyanide, and Total Cyanide (Figures C3.4-8b–f)** – The range of concentration of these COIs in TZW and sediment was generally similar across the two groundwater discharge zones and the low-to-no groundwater discharge zone. As with other COIs in TZW offshore of the Gasco site, the upper end of the concentration range of several of these COIs was slightly lower in the offshore discharge zone than in the zones closer to shore. The TZW concentrations across all four zones were similar to or slightly lower than the concentration ranges observed in the in-river and nearshore upland groundwater samples.

C3.4.5 Groundwater Pathway Assessment for the Gasco Site

Based on an integrated analysis of all of the lines of evidence presented for the Gasco site, the study produced the following findings with respect to the groundwater pathway at the site:

- **Variable Nearshore Groundwater Discharge Zones** – The study identified areas of variable nearshore groundwater discharge, as anticipated by stratigraphic cross sections that indicate discharge could occur in areas where underlying nearshore silt layers are absent. Seepage meter measurements and COI concentrations from in-river groundwater samples are consistent with variable discharge in the nearshore area, with two nearshore locations indicating higher rates of discharge and one indicating low-to-no discharge.
- **Low-to-No Groundwater Discharge Zone** – Seepage meter measurements in this zone indicate low-to-no discharge. Based on findings at the adjacent Siltronic site, this intermediate-depth zone might be expected to be a low-to-no groundwater discharge zone. As discussed previously in Section C3.4.3.3, the

detection of chemicals present in upland groundwater (e.g., total cyanide) in in-river groundwater and TZW samples within this zone may be attributable to transport from upland groundwater sources or from direct discharge of liquid wastes to the river.

- **Offshore Groundwater Discharge Zone** – The offshore groundwater discharge zone was identified based on stratigraphic understanding of the site, the relative depth and projected expression of upland groundwater COIs, and the detailed work done at the adjacent Siltronic site to identify the stratigraphic interval corresponding to this zone as an area of groundwater discharge. NW Natural’s in-water investigation indicated the presence of site-related groundwater COIs in TZW samples from this area, but at generally lower concentration ranges than in TZW collected from discharge zones closer to the shoreline.

Near-bottom surface water samples, collected in 2007 as part of Gasco’s offshore investigation report (Anchor 2008), also provide a line of evidence with respect to the groundwater pathway at the site. As described previously, among the 60 near-bottom surface water samples collected from 20 locations under three different tidal conditions, total cyanide was detected at three locations. (Free cyanide was not detected in any surface water samples.) Of the samples in which total cyanide was detected, one (GSW-14) was collected from the offshore groundwater discharge zone, one (GSW-09) was collected near the boundary between the low-to-no groundwater discharge zone and the offshore discharge zone, and the third (GSW-01) was collected from a downstream reference location. Because surface water samples are collected from a flowing water column, they provide little or no information of specific locations of cyanide discharges from TZW to the water column. Taken together, however, the detections of total cyanide in three of 60 near-bottom surface water samples provides evidence of a complete, but minor, transport groundwater transport pathway for cyanide to the water column.

Overall, the findings of the in-water investigations at the Gasco site suggest that VOCs, PAHs, and total cyanide in upland groundwater are migrating to the transition zone in some areas. However, the concentrations of COIs in TZW are generally comparable in areas of groundwater discharge to areas where low-to-no groundwater discharge is taking place. As a result, the relative contribution of the groundwater transport pathway to COI concentrations observed in the TZW is uncertain due to the masking effects of existing in-water sediment chemical sources, which likely exert considerable influence on the concentrations of COIs in TZW.

C3.5 SILTRONIC

The Siltronic site is located on the western shore of the Willamette River at approximately RM 6 (Figure C1.3-1). The 85-acre site is in an area zoned as Heavy Industrial and is surrounded on three sides by industrial properties. The Northwest Natural Gas Company Gasco (aka Pacific Gas and Coke [PG&C]) facility adjoins the Siltronic site to the northwest (Figure C3.5-1). Berms of the Burlington Northern–Santa Fe (BNSF) Railroad are located immediately adjacent to the site along its southeast and

southwest sides. Beyond the berms are the Star Link Logistics (SLLI, aka Aventis Crop Science, aka Rhone Poulenc AG Company), ESCO Corporation, Gould-NL Industries, and Arkema sites.

Siltronic manufactures silicon wafers from silicon crystal ingots. Currently, all ingots are shipped to the Portland facility from Germany or purchased from other sources. Prior to 1900, the property was undeveloped lowlands. A portion of the property contained part of a small, shallow lake known as Doane Lake. Western Transportation constructed a tug refueling dock at the eastern corner of the property that operated until the 1930s. PG&C excavated and maintained numerous waste disposal ponds from about 1940 through 1967 along the northwestern property boundary. The remainder of the site was mostly undeveloped until it was filled to about 30 feet above msl (current grade) between 1971 and 1977.

A detailed discussion of the Siltronic site, including discussion of historical releases, source areas, and remedial measures is presented in the CSM site summary for Siltronic (Integral 2007a).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the Siltronic site are presented in Table C3.5-1.

C3.5.1 Nature and Extent of Contamination

Historical sources of COIs in soil, groundwater, and other environmental media at the Siltronic site, along with the release mechanisms (when known), include the following (Integral and GSI 2004): potential Western Transportation releases, former PG&C ditches and ponds, PG&C MGP waste incorporated into site fill, impacted Willamette River sediments incorporated into site fill, former Koppers waste disposal via drainage ditches or City of Portland Outfall 22C, disposal or release of pesticide products or by-products to North Doane Lake, potential releases from the Olympic pipeline, release of trichloroethene (TCE) from USTs, MTBE in groundwater associated with Kinder Morgan Pumping Station, and mono- and dichlorobenzenes and Silvex in groundwater associated with the former Rhone Poulenc site.

DNAPL characteristic of MGP waste has been identified at the site (Figure C3.5-2a). The MGP DNAPL contains up to 11 percent by weight naphthalene, as well as PAHs and aromatic volatile compounds. Concentrations of TCE detected in a boring located about 500 ft inland from the riverbank (and adjacent to the former UST area) have approached approximately 58 percent of the solubility of the compound in water, suggesting the possibility of a NAPL source; however, no direct observation of TCE NAPL has been observed in explorations completed to date (Integral and GSI 2004).

Primary COIs in upland groundwater at the site are halogenated VOCs (primarily TCE and degradation products) and chemicals associated with manufactured gas production (BTEx, PAHs, and metals). The distribution of selected COIs in upland groundwater

and TZW at the site is shown in Figures C3.5-2b–e. For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater sampling data collected prior to the 2005 implementation of the GWPA. Figure C3.5-3 presents the distribution of total BTEX in site groundwater along a stratigraphic cross section oriented perpendicular to the river (Figure C3.5-1). Figures C3.5-4a–f present cross sections prepared by MFA (2005) that depict the vertical distribution of TCE, cis-1,2-dichloroethene (DCE), and vinyl chloride in groundwater along multiple section lines (Figure C3.5-4a provides the locations of the section lines). MFA (2005) provides a detailed description of the distribution of these compounds in groundwater and TZW at the Siltronic site.

Higher concentrations of COIs tend to occur in groundwater beneath the western portion of the site, near the common site border with the Gasco site. Vertical profiling of groundwater COI concentrations with depth through the alluvial zone suggest that much of the COI mass is migrating at depth, often below the river bottom. Groundwater containing naphthalene, PAHs, BTEX, cyanide, and some metals is primarily associated with the surficial fill; however, the impacts from these constituents extend deeper on the northwestern margin of the site, toward the PG&C Gasco site.

A plume of TCE and its degradation products, including cis-1,2-DCE, isomers of DCE, and vinyl chloride, is present in shallow and intermediate-depth groundwater beneath the Siltronic property. Based on the exploratory data, the vertical extent of this TCE plume appears to be limited to between about 80 and 140 ft bgs at the downgradient edge. A second, deeper plume containing TCE and its degradation products has been identified in the base of the alluvial aquifer and the CRBG bedrock. This plume is referred to as the offsite TCE plume. The vertical extent of the offsite TCE plume appears to be between 166 to at least 207 ft bgs and also appears to be separate from the shallower TCE plume based on the absence of TCE and its degradation products in samples collected at elevations between the two plumes. Further, the offsite TCE plume is distinguished from the shallower TCE plume by the presence of the offsite COIs including Silvex, an organochlorine herbicide, and MTBE, which may be associated with Kinder Morgan Pumping Station (Integral and GSI 2004).

C3.5.2 Completed and Ongoing Remedial Measures

During construction of the FAB 2 building in 1995, soils contaminated with BTEX, naphthalene, PAHs, tar residue, and high-carbon solids were encountered. Approximately 5,490 tons of contaminated soil were segregated and thermally treated onsite consistent with Petroleum Contaminated Soil Treatment Permit No. PCSLA-NWR-95-004 (the PCST Permit) obtained from the DEQ.

In 2006, Siltronic implemented a pilot test of enhanced *in situ* bioremediation (EIB) at the riverbank and in the source area. The riverbank EIB area was located along the primary groundwater flow axis (i.e., coincident with WS-11-125, see Map C3.5-2c). The EIB reduced concentrations of TCE and its degradation products along the main axis of the chlorinated volatile organic compound (CVOC) plume to non-detect within

approximately one year (MFA 2007). Based on this assessment, DEQ selected EIB to be applied in the source area, and Siltronic completed injection of the EIB treatment media in July 2009 (DEQ 2010). Groundwater monitoring is ongoing to assess the effectiveness of the EIB source control measures.

Natural attenuation has continued to reduce concentrations of TCE and its degradation products throughout the plume and specifically at the riverbank. Recent monitoring from new and existing wells located along the riverbank indicates that concentrations of these compounds are significantly lower than the 2005 data used to evaluate the groundwater pathway. TCE concentrations range from non-detect to approximately 10 µg/L; cis-1,2-DCE concentrations range from approximately 1 to 2,250 µg/L, and vinyl chloride concentrations range from non-detect to approximately 1,610 µg/L. These data, along with the other lines of evidence discussed herein, indicate that while the groundwater pathway continues to be complete, the benefits of natural attenuation are significantly reducing the contribution of TCE and its degradation products from the uplands.

Siltronic and NW Natural Gas are coordinating implementation of upland source control using hydraulic containment, and anticipate that the system will be operational at the time this RI Report is completed. This hydraulic containment is designed to immediately interrupt the groundwater pathway, thereby rendering it an incomplete pathway.

C3.5.3 Groundwater Discharge Pathway Assessment for the Siltronic Site

The following presents a multiple-lines-of-evidence-based assessment of the groundwater discharge pathway at the Siltronic site. This evaluation considers multiple sources of information and data for the site (e.g., stratigraphic and hydrogeologic data; chemical concentrations in groundwater, TZW, and sediment), and draws heavily upon the findings of two “in-river” investigations:

- In-river characterization efforts completed by Siltronic in 2004–2005 (MFA 2005)
- The LWG R2 Groundwater Discharge Mapping and TZW Sampling Investigation completed in 2005.

In September and October 2004, Siltronic collected samples of sediment, TZW, and deep groundwater samples from eight borings located in the Willamette River. These data, coupled with data collected by the LWG that indicated that deeper sediments (i.e., greater than 30 cm bml) were impacted by TCE and vinyl chloride, suggested there was a potentially complete exposure pathway from the upland TCE groundwater plume to the Willamette River. In response, Siltronic completed a supplemental investigation to evaluate this potential pathway. This investigation included sampling surface water from immediately above the Willamette River mudline, TZW, shallow groundwater, and deep groundwater. The work also included sampling soil and groundwater from upland borings along the riverbank. Groundwater elevations were also measured to further characterize vertical hydraulic gradients. MFA also evaluated the chemical fingerprint (based on

tentatively identified compounds using mass chromatograms) of selected upland and in-river groundwater samples. The results of the Siltronic 2004–2005 investigation are presented in MFA (2005).

The LWG 2005 groundwater discharge mapping investigation at the Siltronic site was performed in accordance with the Discharge Mapping FSP (Integral 2005c) to help focus the subsequent TZW sampling effort. In all, 29 in-river measurements were made with the Trident probe. The Trident probe collected temperature and conductivity data above and below the sediment surface, as well as sediment texture information. Additionally, ultrasonic seepage meters were installed for 24-hr periods at six of the Trident locations offshore of the Siltronic site. The mapping locations focused on the nearshore area across the length of the site to better understand the extent of the silt layer in this area and evaluate its effect on shallow groundwater discharge. In addition, samples of TZW were collected from five of the Trident locations (SLT1-B, SLT2-A, SLT3-A, SLT4-A, and SLT5-A) for screening of TCE, TCE degradation products, and BTEX as indicators of groundwater discharge.¹⁶ Detailed results of the discharge mapping are presented in SAP Addendum 1 (Integral 2006a). The findings of the TZW sampling are presented in RI Section 5.

C3.5.3.1 Site Hydrogeology and Groundwater Flow

Figure C3.5-3 presents a stratigraphic cross section that is representative of the general site stratigraphy extending from upland into the river. Additional stratigraphic cross sections are presented in Appendix A-5 of the SAP (Integral et al. 2005) and Addendum 1 to the TZW FSP (Integral 2006a). The general site stratigraphy at the Siltronic site largely parallels that of the Gasco site (see Section C3.3.3.1) and consists, from the ground surface downward, of the following:

- **Surficial Fill** – The surficial fill unit consists of the fill material that was placed on the Siltronic property in the 1970s. The fill unit is generally about 20 to 30 ft thick, but may be thinner near the western/southwestern corner of the property. The surficial fill contains MGP waste as well as potentially impacted Willamette River dredge spoils.
- **Silt Unit** – The silt unit is a laterally discontinuous, fine-grained unit underlying the surficial fill. Where observed, the silt unit may act as an aquitard. This unit consists of up to about 70 ft of silt at WS-10, transitioning to thinner (i.e., about 1-ft to 3-ft-thick) layers of interspersed silt, sand, or silty sand toward the Willamette River (Figure C3.5-3). This silt unit discontinues offshore between borings GP-28 and GP-32.
- **Alluvial Water-Bearing Zone** – The lower, alluvial water-bearing zone (AWBZ) consists of sand with lenses or layers of silt, sandy silt, and silty sand. The AWBZ

¹⁶ Collection of TZW samples for screening analysis was attempted at eight locations; however, three locations (SLT2-C, SLT3-B, and SLT4-C) yielded inadequate flow rates (<2 mL/min) to prevent loss of volatiles during VOC sample collection.

may be as much as about 170 ft thick based on the lack of distinction between this unit and the overlying silt unit in the northeastern portions of the site. The AWBZ is divided into upper, intermediate, lower, and basal units, based on the screen locations of the monitoring wells. The basal AWBZ, which extends from about 161 ft bgs to the top of the CRBG, includes a layer of gravel (ranging from angular to rounded) mixed with silt and sand, ranging in thickness from 0.5 to 33 ft (MFA 2004).

- **Basalt** – Basalt characteristic of the CRBG has been encountered beneath the AWBZ at approximate depths of 100 to 200 ft bgs. The surface of the basalt appears to be gradually dipping toward the north of the site and has continuous contact with the basal AWBZ.

The general direction of groundwater flow is north-northeast toward the Willamette River (Figure C3.5-1). Based on water levels measured in 2004, the hydraulic gradient is ~0.02 ft/ft (Integral and GSI 2004). No aquifer testing has been conducted on the site.

The shallowest groundwater flow system beneath the site generally occurs in the base of the surficial fill layer, with the underlying silty sand deposits, where present, acting as a partial aquitard. The shallow groundwater in the surficial fill layer discharges directly to the Willamette River (MFA 2005).

Groundwater also occurs within the AWBZ. The basal AWBZ includes a layer of gravel (Integral and GSI 2004) that appears to be the preferential pathway for offsite migration of COIs. MFA (2005) reports a downward gradient based on water levels observed in direct push borings in the river offshore and suggests that these conditions indicate that the intermediate zone of the AWBZ beneath the river, where most of the TCE impacts have been identified, is recharged by the Willamette River.

C3.5.3.2 LWG 2005 Groundwater Discharge Mapping Investigation

The following presents a summary of the primary findings of the 2005 groundwater discharge mapping investigation completed at the Siltronic site by the LWG. Detailed results of the discharge mapping are presented in Integral (2006a). Section 5 of the RI presents the results of the TZW sampling.

C3.5.3.2.1 Surface Sediment Texture

Figure C3.5-5 presents the interpreted distribution of offshore sediment textures based on the Trident observations, recent core samples, and past sediment sampling events. A notable feature of the sediment texture map is a laterally continuous zone of sand along the shoreline, which extends from transect SLT1 upstream to transect SLT5. This feature is similar to the nearshore sand observed between transects GSC3 and GSC7 at the Gasco site, located immediately downriver (Figure C3.4-4). Farther offshore, the surface sediment texture trends to sandy silt and silt.

C3.5.3.2.2 Trident Probe Temperature Mapping

Figure C3.5-5 presents the Trident Probe temperature mapping results. The Siltronic site displayed the same general patterns as those observed at other sites along the river during the GWPA Pilot Study (Integral 2005d), with the nearshore sands typically showing smaller temperature and conductivity differences and the offshore silts showing greater differences. It is hypothesized that the smaller temperature and conductivity differences observed in sand are the result of greater mixing between groundwater and surface water in coarser- versus finer-grained sediments. Some exceptions to this general pattern were noted. Locations SLT2-C, SLT3-C, and SLT4-A all displayed larger than expected temperature differences when compared to similar locations at the site. These results may indicate areas of higher groundwater flux and a resulting suppression in the effects of mixing with surface water on TZW temperature and conductivity.

C3.5.3.2.3 Indicator Chemical Screening in TZW Samples

Screening samples of TZW were collected for analysis of VOCs at locations SLT1-B, SLT2-A, SLT3-A, SLT4-A, and SLT5-A during the August 2005 discharge mapping field effort. All of these screening sample locations are inshore of areas where impacted TZW was delineated during the Siltronic supplemental investigations (see Section C3.5.3.3). The screening sample results are presented in detail in Integral (Integral 2006a). The data show low concentrations of total BTEX in two of the samples, SLT1-B and SLT4-A (14.1 and 26.8 µg/L, respectively). Other samples had even lower total BTEX results, at or near detection limits, ranging from 0.6 to 2.7 µg/L total BTEX. Results at all screening locations were below detection limits for TCE, 1,2-DCE, and vinyl chloride.

These findings support the understanding of the distribution of COIs in shallow groundwater at the site, and is in agreement with nearshore discharge mapping results. Specifically, location SLT1-B is near the northwest boundary of the site where there are known NAPL sources in the groundwater. Location SLT4-A is located immediately offshore of well P-2, in which 61 µg/L of total BTEX was detected in shallow groundwater. Further, Trident readings indicate that greater relative groundwater discharge may be occurring at location SLT4-A—a finding that was confirmed by collocated seepage meter results (see below).

C3.5.3.2.4 Seepage Flux Measurement

Seepage meters were installed at six of the Trident locations offshore of the Siltronic site: SLT2-A, SLT2-C, SLT2-E, SLT3-A, SLT4-A, and SLT4-B. These seepage meter locations are designated as SLSEEP 2A, SLSEEP 2C, SLSEEP 2E, SLSEEP 3A, SLSEEP 4A, and SLSEEP 4B. Average seepage flux rates observed at each location are shown on Figure C3.5-5. In agreement with Trident mapping results, locations SLSEEP 4A and SLSEEP 2C showed the highest average discharge rates (10.5 cm/day and 5.1 cm/day, respectively). Locations SLSEEP 2A and SLSEEP 3A fluctuated between high relative rates of discharge (positive flux) to high relative rates of recharge (negative flux). As a result, the average specific discharge rates at locations SLSEEP 2A and SLSEEP 3A were not high (0.2 and 0.3 cm/day, respectively), despite the fact that relatively high,

positive maximum specific discharge rates (18.5 and 2.2 cm/day, respectively) were recorded at these locations. Location SLSEEP 4B, which is located in the silt, showed primarily negative flux signals, suggesting that river water may be locally recharging at this location. In contrast, location SLSEEP 2E, which is located offshore in a silt-to-mixed-sand/silt zone, showed a positive average flux of 3.5 cm/day.

C3.5.3.3 Siltronic 2004 and 2005 Supplemental Investigations

The 2004 In-River Sediment and Groundwater Investigation (MFA 2005) included the collection of 48 offshore groundwater samples from eight locations using direct-push sampling methods (Figures C3.5-6a and b). This work was completed offshore of the northeast corner of the site, in the area downgradient of the upland TCE plume. Results of this investigation are summarized below:

- TCE was detected in 25 of the 48 groundwater samples collected at concentrations ranging from 0.35 to 952 µg/L.
- Total BTEX was detected in 38 of the 48 groundwater samples collected. Benzene concentrations ranged from 0.290 to 103 µg/L, ethylbenzene concentrations ranged from 0.20 to 532 µg/L, toluene concentrations ranged from 0.670 to 13.3 µg/L, and xylene concentrations ranged from 0.240 to 168 µg/L.
- Naphthalene was detected in 36 of the 48 groundwater samples collected at concentrations ranging from 1.65 to 12,600 µg/L. Naphthalene was detected in seven of the eight shallow/transition zone water samples.
- Dichlorobenzene (DCB) was detected in offshore groundwater collected from all of the in-river borings at concentrations ranging from 0.25 to 197 µg/L. The shallowest detection was at 74 ft bml at a concentration of 0.85 µg/L, the remaining detections were all below 165 ft bml.
- MTBE was detected in 10 of the 48 groundwater samples collected. Concentrations ranged from 1.81 to 12.4 µg/L. All detections were from greater than 146 ft bml.

The 2005 investigation included sampling surface water from immediately above the Willamette River mudline, TZW, shallow groundwater, and deep groundwater; sampling soil and groundwater from upland borings along the riverbank; measurement of groundwater elevations to further characterize vertical hydraulic gradients; and chemical fingerprinting of selected upland and in-river groundwater samples (MFA 2005). The results of this investigation, as described in MFA (2005), include the following:

- The vertical gradient beneath the Willamette River is generally downward. The portion of the Willamette River offshore of Siltronic is generally a losing reach. Surface water recharges groundwater.
- TCE and its degradation products were not detected in groundwater more than approximately 450 ft offshore of the Siltronic property, nor were they detected more than approximately 200 ft downstream of the Siltronic property.

- Benzene and naphthalene were detected well above risk screening levels approximately 450 ft from shore (GP74). The elevated levels of these chemicals suggest that these impacts extend significantly farther.
- TCE and its degradation products were detected in TZW samples above risk-based screening levels in two separate and distinct areas. Area 1 is generally located offshore of upland monitoring well WS-12-125/161 [RI Figure C3.5-6a]. Area 2 is located downstream of Area 1 and offshore of upland monitoring well WS-14-125 [RI Figure C3.5-6a].
- The chemical fingerprint of the groundwater samples collected from Area 1 is similar to that observed in upland samples collected at the riverbank and in the former UST area indicating that shallow in-river impacts in this area are related to the upland plume that originated in the UST area.
- The chemical fingerprint of the groundwater samples collected in Area 2 is significantly different from the Area 1 and upland groundwater samples and indicates that the impacts in Area 2 are not part of the groundwater plume that has its origin in the upland portion of the Siltronic property.
- The vertical extent of TCE and its degradation products in groundwater in Area 2 is significantly shallower than in Area 1 and is separate from the upland plume.
- The shallow vertical profile data confirm that Areas 1 and 2 represent different sources of TCE and its degradation products. Specifically, the vertical distribution of TCE in shallow groundwater and TZW in Area 1 is consistent with groundwater interacting with surface water. The vertical distribution of TCE in Area 2 is different from Area 1 and suggests a different source.
- cis-1,2-DCE and vinyl chloride were detected in a limited number (n=1 of 7 and n= 5 of 7, respectively) of Area 1 near-bottom surface water samples. The single detection of cis-1,2-DCE was at a concentration of 1.24 µg/L. The detected concentrations of vinyl chloride ranged from 0.32 to 0.76 µg/L. All of the detected concentrations in Area 1 were below the risk-based screening levels established in MFA (2005).
- TCE, DCE isomers, and vinyl chloride were detected in several near-bottom surface water samples collected within Area 2. TCE was detected in two of 13 samples ranging from 0.61 µg/L (GP69) to 194 µg/L (GP68). cis-1,2-DCE was detected in four of 13 surface water samples ranging from 3.28 µg/L (GP83) to 279 µg /L (GP64). Vinyl chloride was detected in eight of 13 samples at concentrations ranging from 0.46 (GP73-SW) to 73.2 µg /L (GP64-SW). The Area 2 results indicate that impacts to surface water from impacted TZW are spatially limited to within approximately 40 feet of the impacted TZW.

Based on these results, MFA (2005) concluded:

1. “Area 1 represents the in-river expression of the upland plume of TCE (primarily degradation products) originating from the former UST area.”

2. “Area 2 represents a separate, localized source of TCE and its degradation products unrelated to the upland TCE plume or another upland source of contamination. It does not appear that the TCE impacts in Area 2 are related to an ongoing release.”
3. “Impacted TZW results in TCE and its degradation products migrating to surface water at concentrations above screening levels at discrete locations near Area 2, but not Area 1.”
4. “The Area 2 results are significantly different from the Area 1 results in that the concentrations of TCE and its degradation products are higher and concentrated in a smaller area. Within Area 2, the concentrations of TCE (not only relative to the degradation products, but also overall) are greater than within Area 1. Furthermore, the Area 2 concentrations are higher than the concentrations observed upland and in the former UST area, which confirms that they are not related to groundwater transport from the source.”
5. “The nature and extent of MGP-related impacts to the Willamette River (including groundwater, TZW, surface water and sediments) requires further characterization.” (Note that additional characterization was completed as part of NW Natural’s 2007-2008 investigation at the adjacent Gasco site; see Section C3.4.3.3.)

C3.5.3.4 Interpretation of Groundwater Discharge Zones

Based on review of the combined lines of evidence of the groundwater discharge mapping (including review of site stratigraphy, upland groundwater contours and concentrations, sediment texture, Trident temperature results, and seepage meter results), the TZW and sediment analytical chemistry data, and the data presented by MFA (2005), approximate zones of groundwater discharge offshore of the Siltronic site were identified. These zones are indicated on Figure C3.5-7, along with the locations of TZW and sediment samples collected at the site.

Trident temperature, sediment texture, and seepage meter results are consistent with the understanding of the site hydrogeology and suggest that groundwater discharge from the shallow water-bearing zone may be occurring through the nearshore sediments adjacent to the Siltronic site, with variability likely attributable to the varying presence and thickness of the silt layer. This designation is based on the positive average seepage meter measurement of 10.5 cm/day at location SLSEEP-4A. Additionally, BTEX, PAHs, and TPH were detected at relatively elevated concentrations in the nearshore collocated TZW sampling location SL-04-A. BTEX detections were also recorded in the SIR data set (MFA 2005) at nearby nearshore TZW location GP46. The stratigraphic understanding of the site also supports this designation of a nearshore discharge zone.

At intermediate water depths farther offshore, sediment texture mapping and seepage meter results are consistent with stratigraphic information (projection of the silt layer), suggesting lower permeability deposits and reduced groundwater flow rates. COI concentrations in TZW samples from this zone were low relative to other zones, and

seepage meter results (three seepage meter measurements) support designation of a low-to-no groundwater discharge zone.

Farther offshore (i.e., beyond the break in slope that defines the navigation channel), stratigraphic information, Trident temperature mapping, and the results of in-water investigations performed by Siltronic indicate the presence of a deeper groundwater discharge zone. This zone corresponds with where the coarser-grained alluvial zone is expected to project into the river. In this area, positive 24-hr average seepage meter measurements of 5 cm/day and 3.5 cm/day were recorded. Additionally, the COI concentrations in this zone are substantially higher than in the adjacent designated low-to-no flow zone.

At the majority of the locations evaluated in the deep groundwater discharge zone identified in Figure C3.5-7, Siltronic reported a downward vertical gradient based on observed water levels in the offshore borings. These findings suggest that groundwater discharge in this zone is variable and, as MFA (2005) concluded, this portion of the river is predominantly a losing reach.

C3.5.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

Based on the discharge mapping results, a total of 13 TZW samples were collected from 11 locations during the GWPA investigation. Figures C3.5-6a and C3.5-6b show the TZW sampling locations, and Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the Siltronic site. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from depths ranging from 90 to 120 cm at two of the locations. The rationale for selection of the sampling locations was as follows:

- Samples were collected from five locations within the nearshore sand zone at the northern end of the site where the potential for shallow groundwater COI discharge is likely the greatest (SLT1-A, SLT2-A, SLT3-A, SLT4-A, and SLT5-A), based on the seepage data and Trident mapping. A paired sample at a depth of 90 cm was collected at SLT4-A.
- Samples were collected from two locations (SLT2-C and SLT3-C) in the silty area offshore from the nearshore sand unit to assess possible groundwater seepage indicated by seepage meter SLSEEP2C and Trident results.
- Samples were collected from four locations (SLT1-E, SLT2-E, SLT3-F, and SLT4-F) farther offshore near the break in slope to the navigation channel. These locations partially overlap the locations of TZW and offshore groundwater sampling performed by Siltronic in 2004 and 2005. A paired sample at a depth of 120 cm was collected at SLT3-F.

In addition to these samples, 41 TZW samples were collected by MFA as part of an independent Siltronic investigation. These samples are concentrated in the vicinity of

“Area 1” and “Area 2” where elevated concentrations of TCE and its degradation products have been observed.

C3.5.4.1 Major Ion Chemistry

Figure C3.5-8 presents a Piper diagram for the Siltronic site that shows major ion signatures for TZW and upland groundwater at the Siltronic site and compares it to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond shaped plot are linearly scaled from 0 to 2,200 mg/L. In addition, Table 3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the Siltronic site TZW samples was typically -10 percent or less. All of the samples were anion deficient, likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis.

TZW at the Siltronic site and Willamette River water are predominantly calcium-carbonate waters; however, the river water shows a greater influence of sodium and chloride. TZW major ion composition is not significantly different in samples collected from the interpreted zones where groundwater discharge may be occurring than from the samples from the zone where low-to-no groundwater discharge is taking place. These data suggest that the TZW major ion composition is influenced by geochemical interactions within the sediment pore space (e.g., mineral dissolution and precipitation, microbial processes).

Complete major ion data are only available for two upland groundwater samples from the Siltronic site. The two samples show significantly different anion signatures, with one sample being bicarbonate-rich (similar to the TZW and river water) and the other showing a considerable influence of chloride and higher TDS.

C3.5.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figures C3.5-9a–e present the range in concentration of total BTEX, TCE, cis-1,2-DCE, and vinyl chloride observed in TZW and sediment samples collected from the groundwater discharge zones and the low-to-no groundwater discharge zone. These data are also presented in Table C3.5-1. The TZW concentrations are also compared to the range of concentrations observed in nearshore, upland groundwater and “in-river” groundwater samples (i.e., groundwater samples collected from the aquifer below the transition zone).

- **BTEX (Figure C3.5-9a)** – Overall, the concentrations of total BTEX in TZW from the groundwater discharge zones are similar to the concentrations observed in upland and in-river groundwater samples and are greater than the concentrations measured in samples located in the low-to-no groundwater discharge zone. TZW BTEX concentrations are generally greater in the two offshore discharge zones than the nearshore discharge zone, and are particularly elevated in Area 2. Area 1, which is located somewhat upriver of the area of upland MGP impacts, shows lower BTEX concentrations. Sediment BTEX

concentrations were similar in samples from the two offshore groundwater discharge zones to those in samples from the low-to-no groundwater discharge zone. No sediment BTEX data are available for the nearshore groundwater discharge zone.

- **Total PAHs (Figure C3.5-9b)** – The total PAH concentrations in TZW samples collected from the low-to-no and nearshore groundwater discharge zones were comparable and were within the range of the concentrations observed in upland groundwater. However, the in-river groundwater samples exhibited a wider range of total PAH concentrations, and several of the in-river groundwater samples had concentrations that were considerably greater than those observed in the low-to-no and nearshore groundwater discharge zones. Similarly, several of the TZW samples from the offshore groundwater discharge zone exhibited elevated total PAH concentrations relative to the TZW samples collected elsewhere at the site—including all of the samples from Area 2. Total PAHs in sediments exhibited a consistent range of concentration across all groundwater zones sampled.
- **TCE, DCE, and Vinyl Chloride (Figures C3.5-9c–e)** – The concentrations of TCE and its degradation products in TZW samples from the offshore groundwater discharge zones were similar to those measured in upland and in-river groundwater samples. The concentrations of these COIs tend to be the greatest in Areas 1 and 2. MFA (2005) concluded, based on an analysis of the TZW, groundwater, and other data collected during the Siltronic’s 2004 and 2005 in-river investigations, that there is a complete discharge pathway of TCE and its degradation products to Area 1 in the deep groundwater discharge zone (Figures C3.5-6a and C3.5-7). MFA (2005) concluded that Area 2 (Figures C3.5-6b and C3.5-7) represents a separate, localized area of TZW with elevated concentrations of TCE and its degradation products that is unrelated to the upland TCE plume or another upland source of contamination. The concentrations of MGP-related COIs (e.g., PAHs, BTEX, naphthalene) were also elevated in TZW collected from Area 2. It is uncertain if the elevated MGP-related COIs in Area 2 are related to groundwater discharge or chemical partitioning from impacted sediments.

TCE and its degradation products were detected at low concentration or were below detection limits in the TZW samples located in the low-to-no groundwater discharge zone and the nearshore groundwater discharge zone. Further, the concentrations of these chemicals were low or below detection in all of the sediment samples regardless of location relative to groundwater discharge zones.

C3.5.5 Groundwater Pathway Assessment for the Siltronic Site

Based on an integrated analysis of all discharge mapping and sampling results, and the results of the supplemental investigation report (MFA 2005), nearshore and offshore groundwater discharge zones were identified, separated by an intermediate zone of low-to-no groundwater discharge (Figure C3.5-7). Concentrations of VOCs and several PAHs in TZW and sediment are substantially higher in the offshore groundwater

discharge zone than in the nearshore and intermediate zones. There are two primary focus areas of elevated TZW concentrations in the offshore area. As suggested by MFA (2005), it is probable that the source of the chlorinated VOCs in the northwest focus area (Area 2) is not upland groundwater. The focus area to the southeast (Area 1), however, is interpreted to be a probable expression of upland, deep groundwater flow based on stratigraphic considerations, projection of the upland groundwater plume along the groundwater flow path, and the chemical signature of VOCs observed in samples of TZW and offshore groundwater. In the nearshore groundwater discharge zone, BTEX, TPH, and PAHs were observed in the TZW samples at concentrations similar to the intermediate low-to-no discharge zone; TCE and its degradation products were generally undetected in TZW samples from the nearshore zone.

Near-bottom surface water data collected as part of the Siltronic supplemental investigation (MFA 2005) provide an additional line of evidence supporting the existence of a complete groundwater pathway. Detections of TCE and its degradation products in surface water samples from Areas 1 and 2 suggest the existence of complete groundwater transport pathways in these areas. In Area 1, surface water concentrations were low (i.e., below the screening thresholds established in MFA [2005]). In Area 2, surface water impacts were limited in extent to less than 40 ft downstream from areas where impacts to TZW were observed.

C3.6 RHONE POULENC

The Rhone Poulenc site is a former chemical manufacturing facility located at RM 7.2 (Figure C1.3-1), approximately 1,500 ft southwest from the shoreline (Figure C3.6-1). The former Rhone Poulenc manufacturing facility was operational from 1943 to 1990. Products were stored in aboveground and underground storage tanks and in other storage areas. A general production chronology is summarized below:

- Early production included: railroad right-of-way treatments, fertilizers and inorganic pesticide formulations, and sodium arsenite liquids
- Early 1950s: added formulation of organochlorine insecticides and chlorophenoxy herbicides
- Expanded in 1956 to include manufacture of 2,4-dichlorophenoxyacetic (2,4-D) acid/esters
- 1960: added manufacture of 4-chloro-2-methylphenoxyacetic acid (MCPA) acid/esters and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) esters from purchased 2,4,5-T acid
- 1964: added manufacture of 4-(2,4-dichlorophenoxy)butyric (2,4-DB) acid/esters
- 1969: discontinued formulation of all insecticides
- 1971: bromoxynil products were added to production
- 1976: discontinued production of MCPA

- 1982: discontinued production of 2,4-D and 2,4-DB
- 1990: discontinued production of all products at facility.

The insecticide formulation area is located at the southern portion of the Rhone Poulenc Property and was used for the manufacturing, storage, and formulation of insecticides and their components from 1943 to 1969. All aboveground structures have been removed from the IA; the area is partially paved. The Herbicide Area is located adjacent to and northwest of the IA, and was used for the manufacturing, formulation, storage, and handling of herbicides and their components.

Doane Lake, including the area now referred to as the Rhone Poulenc Site Lake Area, is located north of the Herbicide Area and was affected by a number of industrial activities including oil gasification (ended in 1955) and lead recycling (ended in 1980), chemical manufacturing of herbicides (ended in 1990), production of acetylene gas, recycling of construction debris, silicon chip manufacturing, and storage/distribution of liquefied natural gas, petroleum products, and creosote oil (G&M 1990). Doane Lake was filled from all shorelines (except the shoreline along the raised railroad berm to the north) from the mid-1950s until the mid-1970s, when WDL assumed its present-day configuration. During this time period, Doane Lake was filled in various sections by adjacent property owners with soil and other fill material from different industrial activities. The Lake Area portion of Doane Lake was primarily filled during the 1960s and early 1970s (Integral 2007a). A detailed discussion of the Rhone Poulenc site, including discussion of historical releases, source areas, and remedial actions is presented in the CSM site summary for Rhone Poulenc (Integral 2007a).

In addition, the upland source control investigation for the former Rhone Poulenc site is ongoing, with additional data collection being implemented during summer 2009 to address data gaps. A source control evaluation report is anticipated to be delivered to DEQ in 2010.

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the Rhone Poulenc site are presented in Table C3.6-1.

C3.6.1 Nature and Extent of Contamination

Potential sources of COIs in environmental media at the site are described in Integral (2007a). Areas of contaminated soil and NAPL remain on the Rhone Poulenc property, and serve as a potential continuing source to groundwater (Integral 2007a). Sources of contamination include areas of historical production, handling, and storage areas of chemicals, as well as areas of historical waste disposal.

As described in Section C3.6.3.1 below, three hydrogeologic zones underlie the site: fill/shallow alluvium, alluvium, and Columbia River Basalt. Most of the NAPL is present in the alluvium zone with some occurring in the fill/shallow alluvium. The NAPL is primarily present as DNAPL, with a minor component of LNAPL (Integral and

GSI 2004). The approximate area over which NAPL has been observed or suspected is shown in Figure C3.6-2a.

Primary dissolved-phase groundwater COIs include HVOCs (e.g., 1,2-dichlorobenzene, trichloroethylene), insecticides (e.g., DDT, dieldrin), herbicides (e.g., Silvex, 2,4-D), several metals, and dioxins/furans. These constituents have been detected at the site in all three of the groundwater zones (AMEC 2001, 2008b). A detailed list of constituents detected in groundwater at the Rhone Poulenc site may be found in Integral (2007a).

Measured concentrations for DCB, TCE, Silvex, and dissolved arsenic in upland groundwater and TZW associated with the Rhone Poulenc site are presented in Figures C3.6-2b–e. For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater sampling data collected prior to the 2005 implementation of the GWPA. Figures C3.6-3a–d present the distribution of these constituents along a stratigraphic cross section oriented approximately along a groundwater flow path from the Rhone Poulenc site to the LWR in the vicinity of the railroad bridge (Figure C3.6-1).

For purposes of illustration, VOCs, herbicides, insecticides, dioxins and furans, and metals have been selected to illustrate the distribution of groundwater constituents for the Rhone Poulenc site. The distribution of these select COIs is summarized below:

- **VOCs** – In general, VOCs are encountered along the groundwater flow directions, extending northward and northeastward to distal offsite monitoring wells near the river. Concentrations generally increase with depth toward the distal monitoring wells. DCB and other VOCs (chlorobenzene, benzene, chloroform, TCE, DCE, and vinyl chloride) have been detected in groundwater beneath the Siltronic and Arkema sites, as well as in monitoring wells along the flow path—indicating that VOCs originating from the Rhone Poulenc site have migrated with groundwater considerably downgradient of the Rhone Poulenc site (AMEC 2001, 2008b; ERM 2007).
- **Herbicides** – The extent of herbicides varies based on the constituent. Some constituents, such as 2,4-D, remain highly localized. Others, such as Silvex, extend to offsite distal monitoring well locations. The herbicide constituents that extend to the Rhone Poulenc distal monitoring wells tend to increase in concentration with depth, similar to VOCs, beyond the southern portion of the Lake Area.
- **Insecticides** – Insecticides, including DDT (and co-metabolites DDD and DDE), endrin, and dieldrin, have been detected in offsite distal monitoring wells (AMEC 2008a). Concentrations generally increase with depth at distal locations.
- **Metals** – Metals in groundwater do not show any specific patterns or trends. Metals are also detected at background concentrations in wells upgradient of the Rhone Poulenc site.

- **Dioxins/Furans** – Dioxins/furans have been detected in offsite downgradient monitoring wells on the Siltronic and Arkema sites. Concentrations generally increase with depth at distal locations.

A spring 2009 groundwater monitoring program being conducted by Rhone Poulenc will in part provide confirmatory sampling results for past detections of DDT and dioxins/furans.

C3.6.2 Completed and Ongoing Remediation Activities

Groundwater extraction and treatment have been conducted in the Herbicide Area since the early 1980s. Groundwater is extracted from the fill/shallow alluvium and alluvium zones and is treated in an onsite water treatment system that includes biological treatment followed by activated carbon adsorption prior to discharge to the river. Portions of the Rhone Poulenc site, including the Herbicide Area and Insecticide Area, have been paved to minimize the potential for constituents in surface soil to be entrained in stormwater runoff. Since 1984, stormwater has been collected and treated before discharge to the lower Willamette River (LWR).

According to the September 2010 DEQ Milestone Report (DEQ 2010), Rhone Poulenc completed a comprehensive source control evaluation in 2008 and, since that time, has been collecting additional hydrogeologic information to strengthen the site conceptual model and support source control evaluation and design efforts. This has included an extensive groundwater pumping test to support the design of a source control measure to control groundwater contaminant migration in the highly conductive weathered basalt zone beneath the site. Implementation of this source control measure is anticipated in 2011. Additionally, in 2009 and 2010, Rhone Poulenc cleaned and lined the entire length of the Outfall 22B storm sewer to address groundwater exfiltration and transport to the river.

C3.6.3 Evaluation of Groundwater Discharge

In 2005, groundwater discharge mapping was performed at the Rhone Poulenc site, in accordance with the Discharge Mapping FSP (Integral 2005c), to support the evaluation of active groundwater discharge zones associated with the site and to help focus the subsequent TZW sampling effort. Detailed results of the discharge mapping are presented in SAP Addendum 2 (Integral 2006b).

The 2005 groundwater discharge mapping effort at the Rhone Poulenc site included stratigraphic coring, transect-based discharge mapping (temperature and conductivity measurement using the Trident probe), collection of screening samples of TZW, and discharge verification measurements using seepage meters. The groundwater discharge mapping effort primarily focused on the area of projected intersection of deeper alluvium and basal gravel with the river, with a number of measurement points located within the navigational channel to identify any deeper discharge. For this site, the nearshore area was not the focus of the discharge mapping effort. Discharge mapping was performed upstream and downstream of the Railroad Bridge near RM 7.

C3.6.3.1 Site Hydrogeology and Groundwater Flow

Lithologic logs of materials collected from upland borings during the numerous site subsurface boring programs, coupled with the stratigraphic data collected from in-river borings during the 2005 investigation (Figure C3.6-4; Section C3.6.3.2.1), provide a comprehensive understanding of the site stratigraphic features that influence the flow of groundwater beneath the site. The site stratigraphy is depicted in the generalized cross section presented in Figures C3.6-2a–d. The cross section location is provided in Figure C3.6-1. Results from the subsurface borings (locations shown on Figure C3.6-4) indicate that the general site stratigraphy from the ground surface downward consists of the following units:

- **Fill/Shallow Alluvium** – The fill/shallow alluvium zone has been defined as a zone with relatively shallow groundwater (generally no more than 30 ft bgs) that appears to function somewhat hydrologically independent of the alluvial material encountered at greater depths. The fill/shallow alluvium zone is generally laterally continuous along the groundwater flow path throughout much of the Rhone Poulenc site and extends to the bank of the river. The fill material consists of variable amounts of sand, silt, clay, organic matter, occasional gravel, and miscellaneous debris. The shallow alluvium underlies the fill material and consists primarily of interbedded sandy silts and silty sands with occasional discontinuous inter-fingered layers or lenses of sand and clayey silt (AMEC 2003).
- **Alluvium** – The alluvium zone has been defined as the intermediate/deep alluvial deposits between ground surface (if the fill/shallow alluvium zone is absent) or the bottom of the fill/shallow alluvium zone, and the underlying basalt, which is typically present at depths of 60–120 ft bgs. The alluvium zone is laterally continuous beneath the Rhone Poulenc site, and generally consists of discontinuous, fine-grained sandy silt and/or silty sand interbedded with clayey silt and silt lenses. At some locations, gravel underlies the fine-grained alluvium material and overlies the uppermost surface of the basalt bedrock. The alluvial gravel is not laterally continuous and generally coincides with the presence of localized depressions on the basalt surface (AMEC 2003). The gravel appears to be the thickest (up to 45 ft) beneath the southeast corner of the Siltronic property, near the river.
- **Columbia River Basalt** - The Basalt Zone has been defined as the crystalline volcanic rock below the alluvial deposits at the Rhone Poulenc site. The Basalt Zone is laterally continuous and slightly undulated throughout the Rhone Poulenc site, and generally is found at a depth ranging from approximately 60–120 ft bgs. Adjacent to the river south of the BNSF railroad, the surface of the basalt is present at depths of -20 to -50 ft msl. North of the railroad, the depth to the top of the basalt increases dramatically and is present at a depth of -170 ft msl at the northern end of the Siltronic site. The extent of fracturing in the basalt at the Rhone Poulenc site varies from very intensely fractured to slightly fractured. The basalt is generally slightly weathered to fresh, with the uppermost surface (mainly

less than 4 ft thick) typically being intensely weathered to decomposed rock, which exhibits soil-like properties.

Groundwater at the Rhone Poulenc site occurs in three hydrogeologic zones: the fill/shallow alluvium zone, the alluvium zone, and the basalt zone. The groundwater flow direction is generally north and northeast toward the river, as shown on Figure C3.6-1. The gravel zone at the base of the alluvium may act as a preferential pathway, sloping north-northeast toward the river (and possibly below the bottom of the channel) and north-northwest toward the Siltronic site at depths below the bottom of the channel.

In nearshore upland areas downgradient from the Rhone Poulenc site, groundwater COIs have been observed primarily in the alluvium zone. Based on this understanding of the site, the alluvium zone discharge to the river at the Rhone Poulenc site is the primary pathway of concern for the GWPA. The average horizontal gradient in the alluvium zone is 0.009 ft/ft based on data from the spring 2002 groundwater monitoring event (AMEC 2003). Hydraulic conductivity (K) data compiled from slug tests and multi-well pumping tests yield an average K of 2.68 ft/day, with a range of 0.01 to 10.7 ft/day in the sands of the alluvium zone. Clays in the alluvium zone are characterized by an average K of 0.06 ft/day, with a range of 0.03 to 0.09 ft/day. No slug tests or multi-well pumping tests have been conducted in the gravels of the alluvium zone.

C3.6.3.2 Groundwater Discharge Mapping Field Investigation

The groundwater discharge mapping was performed upstream and downstream of the Railroad Bridge near RM 7, in accordance with the Discharge Mapping FSP (Integral 2005c), and included the following elements:

- A total of seven stratigraphic cores (plus one replicate core) were collected offshore of the Rhone Poulenc site (Figure C3.6-4) to improve the understanding of the offshore stratigraphy.
- Forty-nine in-river measurements were made with the Trident probe. The Trident probe collected temperature and conductivity data above and below the sediment surface, as well as sediment texture information.
- Ultrasonic seepage meters were installed for 24-hr periods at 10 of the Trident locations offshore of the site.
- Screening samples of TZW were collected with the Trident probe at 10 locations at a depth of 60 cm below the sediment surface interface. Sampling locations were limited to sandier areas, where purge rates could be maintained above 20 mL/min without clogging the intake. Samples were analyzed for the full project suite of VOCs.

The results of these investigation elements are summarized below and are presented in detail in Integral (2006b).

C3.6.3.2.1 In-River Stratigraphic Borings

Core logs from the in-river stratigraphic borings were used to update the stratigraphic cross section presented in Figures C3.6-3a–d, as well as additional cross sections presented in Integral (2006f). The lithologic materials observed in the borings are consistent with the conceptual understanding of the site stratigraphy (Section C3.6.3.1) and the distribution of sediment texture (Section C3.6.3.2.2). Of particular note, the offshore borings shown on the cross sections encountered gravel at depths of 2 to 15 ft bml, which may represent a preferential pathway for the migration of COIs with deep groundwater. The gravel was generally overlain by a thin surficial silt layer, with occasional sand layers below.

C3.6.3.2.2 Surface Sediment Texture

Figure C3.6-5 presents the interpreted distribution of offshore sediment textures based on the Trident observations, grab samples, offshore boring, and past sediment sampling events. In general, the nearshore area consists of sand, which becomes increasingly silty farther from shore. A sandy outcrop area is observed offshore along transects RP2 and RP3.

C3.6.3.2.3 Trident Probe Temperature Mapping

Figure C3.6-5 also presents the Trident probe temperature mapping results. The Rhone Poulenc Trident data indicate a noteworthy temperature signal (increased temperature signal relative to those recorded on the same transect or in the same sediment texture zone) located at RP3-C. The remaining Trident data indicate two other areas with noteworthy, though somewhat more subtle temperature signals—the areas around RP1-C and RP7-B. Seepage meters were placed at each of these three locations for verification, as well as at locations in different texture zones, to determine relative flow in each of these major zones.

C3.6.3.2.4 Seepage Flux Measurement

Seepage meters capable of recording time-series positive and negative flux were installed at 10 of the Trident locations offshore of the Rhone Poulenc site: RP1-C, RP2-D, RP3-A, RP3-C, RP3-E, RP4-D, RP6-D, RP7-B, RP8-B, and RP9-C. These seepage meter locations are designated RPSEEP 1C, RPSEEP 2D, RPSEEP 3A, RPSEEP 3C, RPSEEP 3E, RPSEEP 4D, RPSEEP 6D, RPSEEP 7B, RPSEEP 8B, and RPSEEP 9C. Average seepage flux measurements observed at each location are shown on Figure C3.6-5.

At all three locations with noted Trident temperature signals, positive average seepage records were observed. RP3-C, in particular, had a high positive seepage flux, averaging 14.0 cm/day. Location RP7-B was the next highest, averaging a positive flux of 4.8 cm/day. Lower discharge rates were observed from the silt and mixed sand and silt zones farther offshore of the site, with the exception of location RP4-D, which had an average positive flux of 3.2 cm/day.

C3.6.3.2.5 Indicator Chemical Screening Sample Results

Screening samples of TZW were collected with the Trident probe at 10 of the discharge mapping locations at a depth of 60 cm below the sediment surface interface. Sampling locations were limited to sandier areas, where purge rates could be maintained above 20 mL/min without clogging the intake. Samples were analyzed for the full project suite of VOCs and select herbicides, including Silvex. Herbicides were not sampled at locations RP1-B, RP6-B, and RP8-B due to the inability to collect adequate volume for analysis (as a result of poorly conductive sediments). Figure C3.6-5 summarizes the detected concentration results in the screening sample results for select herbicides, BTEX, chlorobenzene, DCB, and TCE and its degradation products. Complete results are provided in Integral (2006b).

Screening sample results support Trident temperature mapping and seepage meter results. The highest concentrations of Silvex, chlorobenzene, DCB, and vinyl chloride were all observed at RP3-C, where the strongest temperature signal was observed and the highest seepage meter discharge rates were measured. Elevated concentrations were also observed at RP2-E, which is located in the same sandy zone as RP3-C, and at RP7-B, where Trident and seepage meter results also indicated positive groundwater flux. Very low to undetected concentrations were observed in samples collected farther offshore in the mixed sand and silt zone (RP5-E and RP1-E) as well as those from the central nearshore mixed sand and silt zone (RP4-A, RP5-A, RP6-B).

C3.6.3.3 Interpretation of Groundwater Discharge Zones

Based on review of the combined lines of evidence of the groundwater discharge mapping (including review of site stratigraphy, upland groundwater contours and concentrations, sediment texture, Trident temperature results, screening sample results, and seepage meter results) and the TZW and sediment analytical chemistry data, approximate zones of groundwater discharge offshore of the Rhone Poulenc site were identified. These zones are indicated on Figure C3.6-6.

The sandy offshore sediment area to the north of the Railroad Bridge is identified as a groundwater discharge zone and includes positive average seepage meter measurements ranging from 1.4 to 14 cm/day. The area around RP7-B is also identified as a groundwater discharge zone. Adjacent sediment samples G333, C334, G334, C335, and SD078, in which apparent groundwater COIs including chlorobenzene and DCB were detected (results provided in the SCRA, Appendix A3), were used to better define this zone. The Trident data and the results of a seepage meter in the mixed sand and silt zone immediately upstream of this groundwater discharge zone indicate no groundwater discharge. However, the bulk sediment chemistry for several samples in this zone showed detections of apparent groundwater COIs. Based on these results, this area is designated as an “inferred groundwater discharge zone extension.” This zone is grouped with the groundwater discharge zone data sets in the data analyses discussed in the following sections, even though not supported by multiple lines of evidence.

The nearshore area identified as an “inferred nearshore groundwater discharge zone” is differentiated from the two offshore groundwater discharge zones because the two TZW sampling locations in this zone showed no to very low concentrations of groundwater COIs. This zone is therefore not considered to represent a groundwater plume discharge area. Further, upland groundwater monitoring of nearshore wells completed in the fill and shallow alluvium indicates that groundwater COIs are not present in nearshore groundwater at this depth horizon. Areas outside of the three designated flow zones are designated as a low-to-no groundwater discharge zone. This designation is well supported by seven seepage meter results and TZW sample results at RP7-E.

C3.6.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

Based on the discharge mapping results, a total of 11 TZW samples were collected from eight locations. Figure C3.6-6 shows the TZW sampling locations, and Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the Rhone Poulenc site. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from a depth of 90 to 150 cm at three of the locations. Additionally, three bulk sediment samples were collected (at RP3-C, R2-RP-3, and RP7-B) to address sediment characterization data gaps in the vicinity of TZW sampling locations. The rationale for selection of the TZW sampling locations was as follows:

- Samples were collected from four locations (RP-02-E,¹⁷ R2-RP-1, RP-03-C, and RP-03-E) in the offshore zone of sandy surface sediments along transects RP2 and RP3, where the sediment texture, Trident measurements, seepage results, and screening sample results all indicate groundwater discharge. Paired samples at depths of 90 to 150 cm were collected at three of these locations to provide additional information in this area of interest.
- Two samples (R2-RP-2 and R2-RP-3) were collected in the nearshore sandy area. This area is closer to shore than the area where Trident or seepage meter work was performed during discharge mapping, and was selected for sampling based on USEPA’s concern regarding possible upwelling of COIs through more conductive zones, if any, and the reported observation of a milky white substance seeping from the shoreline during low tide at the location corresponding to R2-RP-3 during the Trident work. (As described below, however, analytical results from samples later collected in this area during the TZW sampling program demonstrate that no, or only low, concentrations of COIs were present in nearshore groundwater.)
- A sample was collected at RP-07-B, which corresponds to the location of positive net discharge seepage meter results as well as observation of groundwater COIs in the screening sample.

¹⁷ In accordance with the letter of conditional approval received by EPA on 10/13/05 (EPA 2005b, pers. comm.), RP-02-E and RP-07-E were targeted as far offshore as practicable.

- A sample was also collected at RP-07-E in accordance with the USEPA letter of conditional approval, dated October 13, 2005 (USEPA 2005b, pers. comm.).

C3.6.4.1 Major Ion Chemistry

Figure C3.6-7 presents a Piper diagram for the Rhone Poulenc site that shows major ion signatures for TZW and upland groundwater at the site and compares these compositions to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are logarithmically scaled from 10 to 1,000,000 mg/L. In addition, Table C3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the Rhone Poulenc site TZW samples was typically ± 10 percent or less. Most of the samples were anion deficient—likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis.

Rhone Poulenc groundwater samples and TZW samples from the groundwater discharge zones show considerable variability in major ion composition. With only a few exceptions, the major ion compositions of these waters are distinct from the major ion composition of the Willamette River water. The two TZW samples collected from the low-to-no groundwater discharge zone, on the other hand, resemble the surface water major ion composition. These results suggest that the TZW major ion chemistry in the groundwater discharge zones is influenced by the discharging groundwater composition (and thus consistent with active groundwater discharge), while TZW in the low-to-no discharge zones is predominantly influenced by the surface water composition.

C3.6.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figures C3.6-8a–d present the range in concentration of TCE, Silvex, 1,2-DCB, and arsenic observed in TZW and sediment samples collected from the groundwater discharge zones and the low-to-no groundwater discharge zone. These data are also presented in Table C3.6-1. The TZW concentrations are also compared to the range of concentrations observed in nearshore, upland groundwater samples.

- **TCE and Silvex (Figures C3.6-8a and b)** – TCE and Silvex were each detected in only one TZW sample—a sample from the northern offshore groundwater discharge zone. The concentrations of TCE and Silvex were below detection in the remaining TZW samples from the remaining two groundwater discharge zones and the low-to-no groundwater discharge zone identified at the site. TCE and Silvex were below detection or detected at low concentration in sediment samples from both the groundwater discharge zones and the low-to-no groundwater discharge zone.
- **1,2-DCB (Figure C3.6-8c)** – The range of concentrations of 1,2-DCB in TZW samples from the two offshore groundwater discharge zones was consistent with the wide range of concentrations measured in nearshore upland groundwater. The two highest detected concentrations of 1,2-DCB in shallow TZW were 640 $\mu\text{g/L}$ (Station RPC3) and 270 $\mu\text{g/L}$ (Station RPE3). These samples were both collected

from the groundwater discharge zone north of the Railroad Bridge and are generally consistent with the upper range of concentrations detected in upland groundwater samples. 1,2-DCB was also detected in one of two TZW samples from the inferred nearshore groundwater discharge zone. 1,2-DCB was detected in the majority of sediment samples collected from the offshore groundwater discharge zones, and in a few samples from the nearshore groundwater discharge zone. The concentration of 1,2-DCB was below the detection limit in the single TZW sample from the low-to-no groundwater discharge zone and was below detection or at low concentration in the sediment samples from this zone.

- **Arsenic (Figure C3.6-7d)** – Arsenic was detected at a consistent level in TZW across the three groundwater discharge zones and within the wide range of concentrations observed in nearshore upland groundwater. The single sample from the low-to-no groundwater discharge zone exhibited a similar arsenic concentration to those observed in the TZW samples from the active groundwater discharge zones. TZW and site groundwater arsenic concentrations were slightly higher than the range of the concentrations observed in the background wells. Comparable ranges in arsenic concentrations were observed in sediment across the three groundwater discharge zones and the low-to-no groundwater discharge zone.

C3.6.5 Groundwater Pathway Assessment for the Rhone Poulenc Site

Based on an integrated analysis of all discharge mapping and sampling results, two offshore groundwater discharge zones were identified offshore of the Rhone Poulenc site within which sediment and TZW chemistry indicate the probable existence of a complete pathway for transport of upland groundwater COIs to the transition zone (Figure C3.6-6). This is demonstrated by concentration patterns observed for 1,2-DCB. The highest concentrations of 1,2-DCB detected in shallow TZW (270 and 460 µg/L) are consistent with concentrations measured in upland groundwater; in addition, the concentrations of 1,2-DCB observed in areas of groundwater discharge are higher than those observed in areas of low-to-no groundwater discharge. Analysis of spatial patterns of COI concentrations in bulk sediment chemistry data suggest that the northern groundwater discharge zone may extend a bit farther upriver than would otherwise be interpreted based on the other lines of evidence.

A third groundwater discharge zone, identified on Figure C3.6-6 as an inferred nearshore groundwater discharge area, does not exhibit strong chemical evidence of transport of upland groundwater COIs to the transition zone, other than a single detection of 1,2-DCB at a relatively low concentration in a TZW sample from this zone. These findings are consistent with the understanding of the nature and extent of COIs in upland groundwater, which indicates that groundwater COIs at the Rhone Poulenc site are primarily migrating to the Willamette River in the alluvium and basal gravel zones.

C3.7 ARKEMA

The Arkema site is located along the west bank of the Willamette River at approximately RM 7.5 (Figure C1.3-1). The site, which occupies approximately 55 acres, was an inorganic chemical manufacturing facility from 1941 to 2001. The plant began producing sodium chlorate and potassium chlorate in 1941 in the Chlorate Plant area (Figure C3.7-1). Chlor-alkali operations started at the plant in 1946. Products included chlorine, sodium hydroxide, and hydrogen gas. The pesticide, DDT, was manufactured at the facility from 1947 to 1954. Chemical base stocks used in the DDT manufacturing process included monochlorobenzene (MCB, or chlorobenzene), chloral, and sulfuric acid. Hydrochloric acid production began in 1966 in the general area where DDT was formerly manufactured. This area became known as the Acid Plant area (Figure C3.7-1). Although the Arkema property also includes a large, currently undeveloped area north of the Acid Plant, the GWPA investigation work and this related discussion focuses on groundwater migrating from the developed portion of the site (Lots 3 and 4) to the adjacent river area.

Chemical manufacturing operations at the Arkema site ceased in 2001. Most of the infrastructure associated with the manufacturing processes has been decommissioned and removed. Extensive, ongoing site investigations, as well as soil and groundwater interim remedial actions, have occurred at the Arkema site since 1994. Arkema submitted an application to DEQ in June 1995 to participate in the Voluntary Cleanup Program (VCP). An RI (ERM 2005b) was initiated in 1998 and completed in December 2005. In October 31, 2008, Arkema entered into an Order on Consent to complete source control measures and a feasibility study for the upland portions of the site.

A detailed discussion of the Arkema site, including discussion of historical releases, source areas, and remedial measures, is presented in the CSM site summary for Arkema (Integral 2007a).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the Arkema site are presented in Table C3.7-1.

C3.7.1 Nature and Extent of Groundwater Contamination

Primary COIs in groundwater at the site include several constituents—DDT, its metabolites DDD and DDE, and MCB—that are primarily associated with pesticide manufacturing process residue (MPR), along with perchlorate and hexavalent chromium associated with the Chlorate Plant area.

A residual MCB DNAPL source area is present in the shallow zone within the former Acid Plant area (Figure C3.7-2a). The MCB NAPL source area is present in the form of microglobules rather than as a continuous, pore-filling phase (ERM 2002); consequently, it is not expected to migrate significantly in the NAPL phase. DNAPL has not been

observed in the deep or basalt zones, nor was DNAPL detected in any of the sediment borings immediately adjacent to the Acid Plant area.

Extensive soil and groundwater investigations have been completed at the Arkema site since 1994. An RI report (ERM 2005b) for the site was prepared in December 2005 and accepted by DEQ in 2006. Subsequent to the RI, a number of investigations have been conducted that have supplemented the understanding of the groundwater pathway at the site. A two-phase DNAPL investigation was performed in 2005 and 2006 to delineate chlorobenzene DNAPL in the Acid Plant area (ERM 2006a). A partial round of groundwater sampling for select analytes was performed in 2006 (ERM 2006b), and a more comprehensive round of groundwater sampling was performed in 2007 (ERM 2007).

Figures C3.7-2b–d depict concentrations of MCB, perchlorate and total 4,4'-DDx¹⁸ in groundwater on the Arkema site based on site groundwater sampling conducted in 2003 and 2007 (most recent available data are shown for each monitoring location). Figures C3.7-2e–f separately depict the 2003 and 2007 concentrations of hexavalent chromium in groundwater because, as discussed further below, concentrations dropped significantly between the two monitoring events in response to a groundwater interim remedial measure (IRM) targeted toward this COI. The MCB and DDx plumes overlies each other in the Acid Plant area, and the hexavalent chromium and perchlorate plumes overlies each other in the Chlorate Plant area. The greatest dissolved-phase impacts to groundwater are in the shallow groundwater zone, with decreasing impacts in the intermediate zone and minimal impacts in the deep zone (see Section C3.7.3.1). Detailed descriptions of each plume and its characteristics can be found in the Portland Harbor CSM Update (Integral and GSI 2004).

In addition to the upland investigations, a comprehensive in-river study adjacent to the Arkema site was conducted by Integral (2003), during which sediment and offshore groundwater sampling was performed. MCB and DDT were detected in offshore groundwater—likely associated with the advective movement of MCB in groundwater from the Acid Plant area. It should be noted that the in-water groundwater samples from this effort were unfiltered samples collected using direct-push sampling techniques which, as discussed previously in Section 3.0.3, bias analytical results high for DDx, metals, and other hydrophobic constituents due to entrainment of particulates in the water sample. As such, the in-water and upland groundwater samples are not directly comparable for DDx, metals, and other hydrophobic COIs. The MCB concentrations in offshore groundwater collected outside of the docks were substantially lower than those on the landward side of the docks. MCB concentrations may be from the dissolved-phase migration of MCB in groundwater from the former pond and trench area to the nearshore sediments.

Additional detail is provided in Appendix A-7 of the SAP (Integral et al. 2005).

¹⁸ DDx = the sum of the concentrations of DDT, DDD, and DDE in a given sample.

C3.7.2 Completed and Ongoing Remedial Measures

Several soil and groundwater remedial measures for groundwater at the Arkema site have been evaluated and implemented at the pilot- and full-scale level.

C3.7.2.1 Soil Interim Remedial Measures

The prior soil IRMs are described below in this section.

C3.7.2.1.1 Phase 1 Soil Removal Interim Measure

The Phase I Soil Removal IRM was performed between September and November 2000, and focused on excavation and offsite disposal of DDx-affected soil from the former MPR Pond and trench areas. Excavations were conducted to a maximum depth of 12 ft bgs. A total of approximately 3,800 tons of soil was excavated and removed as part of the Phase I soil IRM. Grading, paving, and stormwater conveyance improvements were installed within the excavated area. Additionally, a temporary surface cover, consisting of a visqueen plastic layer between two layers of geotextile, buried beneath approximately 2 inches of $\frac{3}{4}$ -inch-minus gravel, was constructed in the unpaved area east of the Acid Plant area. Further details regarding the Phase I Soil IRM activities are presented in the *Interim Remedial Measures Implementation Report* (ERM 2001).

C3.7.2.1.2 Phase 2 Soil Removal Interim Measure

The Phase II Soil Removal IRM was completed in November 2001, and focused on the area north of the former Acid Plant area and south of Warehouse No. 2 (Area D). A total of 91 tons of soil was excavated to a maximum depth of 7 ft bgs. Stormwater conveyance improvements and asphalt paving were installed to reduce transport of DDx-affected soil in stormwater runoff. A detailed description of the Phase II soil IRM activities is presented in the *Phase II Soil Interim Remedial Measure Final Report* (ERM 2002).

C3.7.2.1.3 Soil Vapor Extraction Interim Remedial Measure

A soil vapor extraction (SVE) system was installed in December 2000 to extract MCB mass from subsurface soils, thereby reducing MCB concentrations to allow disposal of the soil as a non-hazardous waste during future excavation activities. The system was expanded periodically over the two and a half years of operation and ultimately included five horizontal extraction wells. The horizontal wells were situated approximately 6 ft bgs.

Detailed descriptions of the SVE system installation, operation, and monitoring, including analytical summary tables and laboratory analytical reports, are presented in monthly progress reports and the *Confirmation Soil Sampling Summary Report* (ERM 2003).

C3.7.2.2 Groundwater Source Control Measures

From 2004 to 2006, three groundwater interim remedial measures were performed at the site to treat hexavalent chromium, chlorobenzene (dissolved phase and DNAPL), and

DDx in groundwater (ERM 2004c, 2004b, 2005a). These IRMs are described in the following subsections. Additionally, groundwater source control activities have included preparation of a groundwater source control evaluation in 2008 (Integral 2008) and groundwater source control measure focused feasibility study (FFS) in 2008 (ERM 2008). As part of the FFS, the following supporting tasks were performed: preparation of a 3D groundwater model, performance of a groundwater treatability study, and performance of a geotechnical evaluation (ERM 2008).

In 2009, DEQ recommended the selection of a groundwater pump-and-treat system with an 1,800-ft top-of-bank slurry wall as the preferred source control approach for addressing the combined chlorobenzene/DDT, hexavalent chromium, and perchlorate plumes (DEQ 2010). This plan is currently in the design process, with operational implementation expected in January 2012.

C3.7.2.2.1 Persulfate Pilot Study and Interim Remedial Measure

A persulfate pilot study was conducted in the vicinity of the former DDT manufacturing area, where MCB concentrations in groundwater have historically been the highest observed at the site. The study was initiated to determine the feasibility of persulfate injection on the reduction of MCB mass in groundwater. During the pilot study, residual DNAPL was observed in one of the pilot study monitoring wells. Arkema initiated a DNAPL recovery effort over a three-month period. A small amount of DNAPL (approximately 6 oz.) was recovered during the first sampling effort, but DNAPL was not observed in the recovery well subsequently. As a result, the recovery effort was discontinued. Although the pilot study was suspended to allow for investigation of the residual DNAPL, early results demonstrated that persulfate was a very effective *in-situ* technology for destruction of MCB and DDT in groundwater at the facility. Phase 1 of a full-scale IRM/source control was implemented in September 2005, injecting 5,767 gallons of 2 percent solution at 23 locations, and 70,691 gallons of 15 percent solution at 83 locations.

C3.7.2.2.2 Air Sparge / Soil Vapor Extraction Pilot Study and Interim Remedial Measure

An air sparge (AS)/SVE pilot study was conducted in the Acid Plant area in the location of the highest MCB concentrations observed during the DNAPL investigation (ERM 2004a). The pilot study was conducted to determine the feasibility and effectiveness of coupling air sparging with vapor extraction for remediation of DNAPL and dissolved-phase MCB. The pilot study operated for approximately two months and resulted in the reduction of average MCB concentrations of approximately 64 percent (for the 10 wells sampled as part of the pilot study). Based on the success of the pilot study, a full-scale air sparging/vapor extraction IRM for source control was installed and began operating in December 2004.

C3.7.2.2.3 Hexavalent Chromium Pilot Study and Interim Remedial Measure

A hexavalent chromium pilot study was conducted at the site in the Chlorate Cell Room, the location of the highest chromium concentrations (ERM 2004c). The study involved

the injection of calcium polysulfide to reduce chromium from its hexavalent state to a trivalent state. Results of the study indicate that chromium concentrations decreased by an average of 95 percent approximately 15 weeks after the injection of calcium polysulfide. Because of the success of the study, the technology was expanded, based upon final DEQ approval of the work plan, into a full-scale IRM/source control measure implemented in 2005. Groundwater sampling performed by Arkema in 2007 demonstrated that hexavalent chromium concentrations had been widely reduced across the treatment area (ERM 2007). Average dissolved hexavalent chromium concentrations in the Shallow, Intermediate, and Deep Zones were reduced by 75, 85, and 92 percent, respectively, by this IRM (ERM 2008).

C3.7.2.2.4 *In Situ* Perchlorate Treatability Study

A laboratory bench-scale treatability study was completed in 2006 to investigate the potential for *in situ* bioremediation of perchlorate in site groundwater using microbial populations and a variety of electron donors. Results from this study demonstrated that perchlorate reduction can be achieved, but that bioaugmentation is likely required to achieve successful bioremediation *in situ* at the site (ERM 2008).

C3.7.3 Evaluation of Groundwater Discharge

Groundwater discharge mapping was performed at the Arkema site during both the fall 2004 GWPA Pilot Study and the summer 2005 GWPA field effort to help focus the subsequent TZW sampling. These investigations were performed in accordance with GWPA Pilot Study FSP (Integral 2004) and the groundwater discharge mapping FSP (Integral 2005c), respectively. Detailed results of the discharge mapping are presented in the Round 2 GWPA SAP, Appendix B (Integral 2005d) and Addendum 1 (Integral 2006a).

C3.7.3.1 Site Hydrogeology and Groundwater Flow Patterns

Lithologic logs of materials collected during the numerous site subsurface boring programs provide a comprehensive picture of the site stratigraphic features that influence the flow of groundwater beneath the site. The site stratigraphy is depicted in generalized cross sections (Figures C3.7-3a–d), which were obtained from (ERM 2005b) and Integral (Integral 2003), and amended to extend the interpretation of stratigraphy into the river based on data gathered during the Portland Harbor RI/FS Round 2A sediment boring program. The cross-section layouts are provided in Figure C3.7-1. Upland groundwater sampling data from the 2003 comprehensive sampling event and TZW sampling results from the GWPA are also depicted on these cross sections.

The general site stratigraphy from the ground surface downward consists of the following (ERM 2005b):

- The surficial geology at the site is characterized by fill and alluvial deposits of the Willamette River.

The riverbank area, generally between the No. 1 and No. 2 Docks received miscellaneous fill for many years. Fill was placed in the Acid Plant area bordering the Willamette River after DDT manufacturing ceased. It appears that the bank adjacent to the Acid Plant area has been filled out toward the Willamette River approximately 200 ft since the 1950s. Fill thickness ranges from a few feet in the former DDT manufacturing area to approximately 25 ft along the riverbank (Integral 2007a). The source of the fill is generally believed to be river dredge spoils and deposits from onsite and offsite excavations. This was an accepted practice for nearshore areas of properties along the Portland Harbor.

- The native soil profile is generally characterized by laterally discontinuous, alternating layers of dark gray-brown sand with varying amounts of silt and thinner silt layers with varying amounts of fine sand.
- Underlying the deepest silt layer, at a depth of approximately 35 ft, is a sand layer, with black sands on the northern end of Lots 3 and 4 and dark gray-brown sands toward the southern end of the plant.
- Columbia River Basalt is observed below the fill and alluvium at the site at depths of 50 to 80 ft bgs.

Groundwater occurs in fill materials and four distinct groundwater zones beneath the site: shallow unconfined alluvial aquifer, intermediate confined alluvial aquifer, deep confined alluvial aquifer, and basalt bedrock aquifer. The silts separating the groundwater zones (aquitards) vary in thickness across the site from approximately several inches to approximately 5 ft. The distinct groundwater zones have been observed across the entire site, with the exception of the southeastern portion of the site. In that area, downgradient of the Chlorate Plant area, the silt aquitards tend to become discontinuous, and the shallow and intermediate groundwater zones tend to coalesce. Groundwater in the shallow and intermediate zones flows to the north-northeast (plant east-northeast) in the Acid Plant area and east-northeast (plant east-southeast) in the Chlorate Plant area (Figure C3.7-1). Both zones follow a gradient of about 0.005 ft/ft. The shallow zone is characterized by a slightly higher hydraulic conductivity (average 17 ft/day), while the intermediate zone has a hydraulic conductivity of 5.8 ft/day. The primary pathway for upland groundwater plumes to reach the river is through the shallow aquifer zone present at both the former Acid Plant and Chlorate Plant areas.

C3.7.3.2 Groundwater Discharge Mapping Field Investigation

Groundwater discharge mapping was performed at the Arkema site during both the fall 2004 GWPA Pilot Study and the summer 2005 GWPA field effort to help focus the subsequent TZW sampling. Combined, the groundwater discharge mapping investigations span the shoreline offshore of the Acid Plant and Chlorate Plant areas. Trident measurements were taken at 41 points distributed over 11 transects across the nearshore areas of the former Acid Plant and the former Chlorate Plant. The Trident probe collected temperature and conductivity data above and below the sediment surface, as well as sediment texture information. Additionally, ultrasonic seepage meters were installed for 24-hr periods at 14 locations offshore of the Arkema site (three during the

fall 2004 pilot study and 11 during the summer 2005 field effort). Detailed results of the discharge mapping are presented in SAP Addendum 1 (Integral 2006a).

C3.7.3.2.1 Surface Sediment Texture

Figure C3.7-4 presents the interpreted distribution of offshore sediment textures based on the Trident observations and past sediment sampling events. A laterally continuous zone of sand is evident along most of the shoreline, though it appears to be absent offshore of the Chlorate Plant area in the vicinity of transects CP8 and CP9. Farther offshore, the sediment texture trends toward mixed sand/silt and silt. However, based on stratigraphic data, sandier water-bearing materials may also be in hydraulic communication with the river farther offshore, in the vicinity of and immediately offshore of the dock structures (Figure C3.7-3a).

C3.7.3.2.2 Trident Probe Temperature Mapping

Figure C3.7-4 also presents the Trident probe results as the difference in temperature (°C) between the river water and the sediments (at a depth of 60 cm) from the 2004 pilot study (Integral 2005d). In general, the nearshore sands generally showed smaller temperature differences, and the offshore silts showed greater differences. Apparent exceptions to this general pattern were observed at locations CP-07-B and CP-11-AA, where temperature signals in the nearshore sand were stronger than elsewhere. These exceptions, as discussed in Section 3.0.1, may indicate areas of higher groundwater flux and a resulting suppression in the effects of mixing with surface water on transition zone water temperature.

C3.7.3.2.3 Seepage Flux Measurement

The average seepage flux rates measured at the 11 Round 2 GWPA locations offshore of the Arkema site are presented in Figure C3.7-4. The majority of seepage meters (7 of 11 total measurements) adjacent to the Arkema site revealed a low or negative flux rate, indicating that groundwater is discharging at low to negligible rates. Sandy and silty-sand locations APSEEP 1, APSEEP 5, CPSEEP 10, and CPSEEP 11 displayed high discharge rates relative to other locations, with average specific discharge rates of 4.0, 3.1, 7.0, and 2.1 cm/day, respectively. The maximum specific discharge rates recorded at these locations were 16.0, 17.4, 31.5, and 3.1 cm/day, respectively. All four of these locations are located inshore of the dock structures. The average specific discharge rate at the remaining seven locations was low (<0.5 cm/day) or negative (recharge). The three seepage meters located slightly offshore of the dock structures (APSEEP 3, APSEEP 6, and CPSEEP 9), all recorded near-zero average discharge rates (ranging from 0.5 to -1.2 cm/day).

C3.7.3.3 Interpretation of Groundwater Discharge Zones

Trident temperature, sediment texture, and seepage meter results (Figure C3.7-4) are consistent with the conceptual model of upland stratigraphy and groundwater flow toward the river. Based on review of the combined lines of evidence of the groundwater discharge mapping (including review of site stratigraphy, upland groundwater contours and concentrations, sediment texture, Trident temperature results, screening sample

results, and seepage meter results) and the TZW and sediment analytical chemistry data (see Section C3.7.4 and RI Section 5), approximate zones of groundwater discharge offshore of the Arkema site were identified. These interpreted zones are indicated on Figure C3.7-5.

A nearshore groundwater discharge zone is designated over much of the Arkema shoreline. This zone encompasses a region of primarily sandy surface sediment, and was delineated based on the stratigraphic understanding of the site, analytical results for TZW and sediment, and three nearshore seepage meter measurements ranging from 2.1 to 7.0 cm/day average discharge.¹⁹ The area immediately offshore of the nearshore discharge zone, across the length of the site to the salt dock, is designated as a variable groundwater discharge zone. This zone is present across the area of the projection of the silt unit (interbedded with sand) shown in the stratigraphic cross sections (Figures C3.7-3a–d). This zone extends offshore to the approximate toe of the slope that defines the transition to the channel bottom. Based on stratigraphy, analytical results, and seepage meter measurements, groundwater is expected to discharge through this area at a lower rate than that observed in the nearshore zone. Additionally, it is expected that discharge will be variable, meaning there will be some areas where the silts limit groundwater discharge. This generalization is supported by the seven seepage meter results from the zone, ranging in average seepage rates from -4.5 to 3.1 cm/day, with average seepage rates for four of seepage meter locations being close to zero and for two of the locations being negative. The one positive result (3.1 cm/day) was from APSEEP 5.

Finally, beyond the variable groundwater discharge zone, the area farther offshore is designated as a low-to-no groundwater discharge zone. This designation is based on the stratigraphy and two seepage meter measurements showing no net positive discharge and no strong tidal fluctuations throughout the measurement period.

C3.7.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

Based on the discharge mapping results, a total of 10 TZW samples were collected from seven locations in the Acid Plant area. In the Chlorate Plant area, a total of 10 TZW samples were collected from eight locations. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from a target depth of at least 90 cm (up to 150 cm, where possible) from three locations in the Acid Plant area and two locations in the Chlorate Plant area.

The rationale for selection of the sampling locations (Figure C3.7-5) during the 2005 Round 2 investigations was as follows:

¹⁹ An additional seepage meter (CPSEEP-07-B) in this zone recorded zero discharge; however, this meter was very close to the shoreline, and results are not considered representative of the entire zone. The nearby TZW sampling location (CP-07-B) produced the highest observed concentrations of chloroform in the Chlorate Plant area.

- Samples were collected from seven locations within the nearshore sand and silty sand zone (AP-02-A, AP-03-A, CP-06-A, CP-07-A, CP-07-B, CP-08-B, and CP-09-A). A paired sample (at a depth of 150 cm, if possible) was collected at three of these locations (AP-03-A, CP-06-A, and CP-07-B). These sampling locations are focused on the nearshore areas immediately offshore of the upland COI plumes, where the potential for shallow groundwater (and associated COI) discharge is the greatest.
- Samples were collected from three locations (R2-AP-1, R2-AP-2, and AP-04-C) from intermediate depths inshore of the docks in the Acid Plant area. A paired sample at a depth of 150 cm was collected at R2-AP-2. These are located in the region where the highest concentrations of chlorobenzene and DDT were observed during Arkema's offshore groundwater investigation (Integral 2003), and where recorded seepage rates (APSEEP 5) suggest groundwater discharge may be occurring.
- Samples were collected from five locations (AP-02-D, AP-03-D, R2-CP-1, CP-07-D, and CP-09D) farther offshore near the break in slope to the navigation channel to evaluate potential COI discharge associated with deeper groundwater flow at the site. Paired samples at a depth of 150 cm were collected at two of these locations (AP-03-D and CP-07-D).

TZW samples were also collected from six additional locations, three each in the Chlorate Plant and Acid Plant areas, during the pilot study. Figure C3.7-5 shows the TZW sampling locations, and Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the Arkema site.

C3.7.4.1 Major Ion Chemistry

Figure C3.7-6 presents a Piper diagram for the Arkema site that shows major ion signatures for TZW and upland groundwater at the site, and compares the signatures to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are logarithmically scaled from 10 to 1,000,000 mg/L. In addition, Table C3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the Arkema site TZW samples was typically ± 15 percent or less, although several samples exhibited a greater charge imbalance. The charge balance for the upland groundwater samples from the site is often greater than ± 25 percent, indicating considerable imbalance in the groundwater major ion fingerprint. As a result, there is some uncertainty with respect to the major ion signature for several of the TZW samples and the upland groundwater samples at the Arkema site. In most cases, the TZW and groundwater samples were anion deficient—likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis.

The Arkema groundwater samples and TZW samples from the groundwater discharge zones show considerable variability in major ion composition. The TZW and groundwater major ion signature is distinct from that of the Willamette River water, suggesting that the TZW major ion chemistry in the groundwater discharge zones is not dominated by surface water interactions. However, the two TZW samples collected from the low-to-no groundwater discharge zone also do not resemble the surface water major ion composition. Collectively, this suggests that the TZW major ion composition is influenced by in-water sources and chemical reactions to a greater extent than by discharging groundwater.

C3.7.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figures C3.7-7a–d present the range in concentration of MCB, total DDx, perchlorate, and total chromium observed in TZW and sediment samples collected from the groundwater discharge zones and the low-to-no groundwater discharge zone. These data are also presented in Table C3.7-1. The TZW concentrations are also compared to the range of concentrations observed in nearshore upland groundwater samples.

- **Monochlorobenzene (Figure C3.7-7a)** – MCB concentrations in TZW do not show clear spatial patterns, with both of the groundwater discharge zones and the low-to-no groundwater discharge zone exhibiting a comparable range in MCB concentrations. The MCB concentrations in TZW are in the lower end of the range of concentrations observed in nearshore groundwater. Sediment MCB concentrations vary widely across the site; notably, however, the highest sediment concentrations were measured in the low-to-no groundwater discharge zone, possibly indicating that groundwater transport is not the only source of MCB detected in sediments.
- **Total DDx (Figure C3.7-7b)** – Total DDx was detected in only one filtered push probe TZW sample and one peeper sample offshore of the Arkema site. All other filtered push probe and peeper sample results for total DDx were non-detects. Total DDx was also detected in three unfiltered push probe samples where the collocated filtered samples were non-detect. The detections of total DDx in unfiltered push probe samples is therefore interpreted to be an artifact of DDx bound to particulates introduced during the sampling process.
- **Perchlorate (Figure C3.7-7c)** – The concentrations of perchlorate in TZW in the nearshore and variable groundwater discharge zones are similar to those in upland groundwater, and are considerably higher than the concentrations observed in the low-to-no groundwater discharge zone. Perchlorate was largely below detection in sediment samples at the Arkema site regardless of location relative to the groundwater discharge zones.
- **Total Chromium (Figure C3.7-7d)** – TZW samples exhibited similar ranges of total chromium concentration regardless of location relative to the groundwater discharge zones. Further, the detected TZW chromium concentrations are low

(<11 ppb) and are at the low end of the range observed in upland groundwater even prior to the hexavalent chromium interim remedial measure. As discussed in Section C3.7.2.2.3, concentrations of hexavalent chromium were significantly reduced in upland groundwater during that interim remedial measure. Total chromium concentrations in sediment were generally comparable across the two discharge zones and the low-to-no groundwater discharge zone.

C3.7.5 Groundwater Pathway Assessment for the Arkema Site

Based on an integrated analysis of all discharge mapping and sampling results, nearshore and intermediate variable groundwater discharge zones were identified at the Arkema site (Figure C3.7-5). Farther offshore, a zone of low-to-no groundwater discharge was identified. These zones span the areas offshore of both the Acid Plant and Chlorate Plant at the site. The analysis of TZW and sediment chemistry within the nearshore and intermediate zones indicates a complete pathway for transport of some, but not all, upland groundwater COIs to the transition zone. Of the detected COIs in the TZW, the evidence suggests that a complete groundwater pathway to TZW exists for chlorinated VOCs, perchlorate, and chromium. The possibility is not ruled out that hydrophobic DDx compounds may be transported to the transition zone to a small degree via the groundwater pathway; however, the finding that detectable DDx in TZW appears to be largely an artifact of particulates introduced during sampling suggests that other potential pathways, such as historical overwater releases, are likely more significant.

C3.8 WILLBRIDGE

The Willbridge Terminals site borders the western shore of the Willamette River at between RM 7.5 and 8 and is located in Portland's Northwest Industrial District (Figure C1.3-1). The Willbridge site consists of three adjacent, currently operating terminals for petroleum storage and transfer facilities. The site is bordered by Arkema to the northwest and McCall Oil and former Chevron Asphalt Refinery to the southeast (Figure C3.8-1). Highway 30 (St. Helens Road) is adjacent to Willbridge Terminals to the southwest. Willbridge Terminals includes the ConocoPhillips terminal, the Chevron Willbridge Distribution Center, and the Kinder Morgan Linnton terminal (KMLT).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the Willbridge site are presented in Table C3.8-1.

C3.8.1 Nature and Extent of Groundwater Contamination

The primary sources of COIs detected in soil and groundwater beneath the site appear to be related to releases from ASTs, associated piping, truck-loading racks, rail-loading facilities, and docking facilities that store and transfer petroleum hydrocarbons and other chemicals. Other minor sources of COIs found in soil and groundwater appear to include a limited number of USTs, drums, and other small containers.

LNAPL has been observed in numerous wells at all three facilities (Figure C3.8-2a), but does not appear to be present as a contiguous plume. Dissolved groundwater plumes contain BTEX (Figure C3.8-2b), total PAHs (Figure C3.8-2c), and several metals generally associated with petroleum releases (Figure C3.8-2d depicts the occurrence of total chromium). For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater sampling data collected prior to the 2005 implementation of the GWPA. Nearshore BTEX and total PAH plumes are located primarily beneath the Chevron and ConocoPhillips properties, while metals are present in groundwater beneath all three terminals. Figures C3.8-3a–c present the concentrations of BTEX, total PAHs, and total chromium²⁰ for upland wells on a representative stratigraphic cross section for the site.

The distribution of BTEX constituents in groundwater is similar to the distribution of LNAPL. BTEX concentrations are highest near the southern portion of the Chevron tank farm and the area of the ConocoPhillips and Chevron properties between the river and Front Avenue. Like BTEX, the highest concentrations of lead and chromium are generally found in the area between the river and Front Avenue.

A detailed discussion of the Willbridge site, including discussion of historical releases, source areas, and remedial measures, is presented in the CSM site summary for Willbridge (Integral 2007a).

C3.8.2 Completed and Ongoing Remedial Measures

Soil excavation has been conducted as part of construction projects or responses to accidental releases at the three terminals. These construction activities included the management of petroleum-hydrocarbon-impacted soil, if encountered. Impacted soils have been typically hauled to Hillsboro Landfill or TPS Technologies. No soil excavation has occurred with the specific intent of source control.

In addition, the following remedial measures are ongoing or have been completed at the Willbridge Terminals based on information obtained from Integral and GSI (2004) and Delta (2005b):

- **Containment Booms** – Containment and sorbent booms currently border the shoreline between the Chevron and ConocoPhillips docks and from the south edge of the ConocoPhillips dock to the southern property line (Figure C3.8-1).
- **Cutoff Wall** – A 170-linear-ft cutoff wall was completed in January 2002 to prevent the seepage of NAPL from the backfill material surrounding a 60-inch stormwater outfall to the Willamette River. The construction of a second cutoff wall was completed in 2006 to eliminate the seepage of NAPL and potentially

²⁰ Note: All data for the cross-section plots were taken from Appendix A of the Groundwater Pathway Assessment SAP (Integral et al. 2005).

impacted groundwater from the area of the former 27-inch outfall and Holbrook Slough to the Willamette River.

- **Groundwater Recovery System** – A groundwater extraction and treatment system is currently operating to maintain the groundwater level and recover NAPL behind both cutoff walls. Additional wells are positioned upgradient of the wall along the storm sewer right-of-way to enhance the recovery of NAPL and petroleum-hydrocarbon-impacted groundwater.
- **Holbrook Trench Recovery System** – The Holbrook Trench Recovery System was installed in 1988 to mitigate a NAPL seep at the ConocoPhillips/Chevron property line that resulted in localized sheens on the river. The system operated from 1988 until 1993 when it was shut down due to lack of NAPL recovery. Between 1993 and 2002, only a few sheens of limited extent were noted in the vicinity of the seep. In response to an increase in the frequency of sheens in 2002, the Holbrook Trench Recovery System was reactivated. Because the trench becomes flooded with river water at higher river stages, operation of the recovery system is limited to periods of low river stage. The system operated on an intermittent basis from the summer of 2002 until its removal in 2006 during the installation of the 27-inch outfall cutoff wall. The upland stranded wedge between the new wall and the river was removed by excavation in 2007.
- **Storm Drain Replacement** – In December 2003, a concrete storm drain under the alley separating the Light Products Terminal and the Lubricants Plant at the Chevron facility was replaced with an 18-inch-diameter welded HDPE pipe. A bentonite, CDF cut-off wall with a recovery sump was installed to eliminate NAPL migration in the storm drain backfill material.

According to the September 2010 DEQ Milestone Report (DEQ 2010), two additional groundwater source control evaluations have been initiated at the Willbridge site since the GWPA investigation was completed. These are intended to address potential groundwater contamination in deeper water bearing zones beneath the site. One is being conducted by Chevron/Conoco and was anticipated in the September 2010 Milestone Report to be complete by late 2010. The second is being conducted by Kinder Morgan with an anticipated completion date of the second quarter of 2011.

C3.8.3 Evaluation of Groundwater Discharge

Groundwater discharge mapping was performed at the Willbridge site during the summer 2005 GWPA field effort to help focus the subsequent TZW sampling. This investigation was performed in accordance with the Round 2 Groundwater Discharge Mapping FSP (Integral 2005c). Detailed results of the discharge mapping are presented in the Round 2 GWPA SAP, Addendum 2 to the TZW FSP (Integral 2006b).

C3.8.3.1 Site Hydrogeology and Groundwater Flow Patterns

Figures C3.8-3a–c present a generalized stratigraphic cross section for the Willbridge site amended with the concentrations of selected COIs observed in groundwater and TZW in the vicinity of the cross section.

The following information from Delta (2005b) summarizes the general site stratigraphy:

- **Recent Fill** – The site is located in the historic Doane Lake area. This area once contained several small lakes, including Kittridge and Doane lakes, as well as sloughs. These lakes and sloughs were filled with Willamette River dredge materials. The fill is very loose to medium dense and fine- to medium-grained sand and silty sand. The thickness of the fill material ranges from nonexistent to greater than 30 ft. There is relatively little fill in KMLT’s south tank yard, while there are significant fill areas on the rest of the site.
- **Pleistocene-Recent Alluvium** – In general, the alluvium is very soft to medium stiff clayey silt with sand and organics. The alluvium is often interbedded with silty clays and clays. The alluvium is initially encountered between ground level and depths of 20–30 ft below grade at the site. The thickness of this unit has been explored within the Chevron tank farm. In two geotechnical borings, the alluvium extended from a depth of ~25 to ~50 ft bgs, where basalt was encountered.
- **Columbia River Basalt** – Based on the two geotechnical borings in the Chevron tank yard, basalts of CRBG are present at approximately 50 ft bgs. The Columbia River Basalt flows, which date from the Miocene age, are jointed and usually have rubble or vesicular tops that contain most of the groundwater (Integral and GSI 2004).

A single, unconfined aquifer exists at the site in the dredge sand fill materials and underlying native alluvium. The native alluvium consists predominantly of silt, with some interbedded sand and silt/clay deposits. Groundwater flow occurs primarily in the coarse-grained materials of the fill layer. Due to the dominance of silt in the alluvium, the hydraulic conductivity of this unit likely limits groundwater flow. However, limited interbedded layers of sand have been observed in the alluvium, which may represent local pathways for groundwater flow within the unit. Beneath the native alluvium is the basalt bedrock.

The groundwater gradient is generally east to northeast toward the river, with flow likely occurring predominantly in the higher conductivity sand fill. The contact between the sandy fill and underlying alluvium is near the elevation of the river. Due to a silt ridge in the native alluvium near the river and parallel to the shoreline, which may have been a natural levee for a former lake in the area or a feature of the former Holbrook Slough, the groundwater gradient is relatively flat nearshore over the downstream half of the site and steeper in the upstream part of the site, where the silt ridge may be discontinuous or breached.

Two preferential flow pathways associated with the Chevron and ConocoPhillips terminal areas are present in the upstream half of the site. The first is a former 27-inch wood stave stormwater outfall collocated with the former Holbrook Slough. The stormwater outfall was grouted in 1982 and replaced with a 60-inch stormwater outfall to the southeast, which is the second preferential pathway. A sheet pile cutoff wall with groundwater recovery system was installed in 2006 across the former 27-inch outfall and the former Holbrook Slough. In 2007, seeps were noted from the upland stranded wedge between the new wall and the river. This wedge was removed by excavation in 2007. No seeps have been noted since the installation of the wall and the removal of the stranded wedge. A cutoff wall and recovery system were installed around the 60-inch outfall to intercept preferential groundwater plume migration in the area. In 2007, petroleum sheens were noted discharging from the 60-inch outfall. The source of the sheens has been identified as infiltration at joints in the sewer pipe. A liner is scheduled to be installed in the 60-inch pipe in summer 2009 to mitigate infiltration.

Three seep areas are present at the site: two near the Kinder Morgan dock, and one (discussed above) on the property line between the Chevron and ConocoPhillips terminals. BTEX and PAHs had been detected in the seep on the property line between the Chevron and ConocoPhillips terminals, which is now contained by the installation of the cutoff wall and removal of the stranded wedge. Metals, including mercury and zinc, have been detected at the two seeps near the Kinder Morgan dock.

Based on this information, potential discharge areas for groundwater-related COIs to the Willamette River include the nearshore areas along the shoreline of the site, with particular focus on the area between the Chevron and ConocoPhillips docks where groundwater gradients are higher, dissolved groundwater plumes are close to the shoreline, preferential pathways are documented, and a seep has been observed to contain groundwater COIs.

C3.8.3.2 Groundwater Discharge Mapping Field Investigation

In 2005, discharge mapping was performed at the Willbridge site in accordance with the Discharge Mapping FSP (Integral 2005c) to help focus the subsequent TZW sampling effort. In all, 38 in-river measurements were made with the Trident probe (Figure C3.8-4). The Trident probe collected temperature and conductivity data above and below the sediment surface, as well as sediment texture information. Ultrasonic seepage meters were installed for 24-hr periods at seven of the Trident locations offshore of the site. Additionally, five offshore stratigraphic cores (plus one replicate core) were collected to improve the understanding of the offshore stratigraphy. Core logs were used to update the stratigraphic cross sections. The groundwater discharge mapping effort spanned the entire shoreline, extending both upstream and downstream of the site boundaries.

Detailed results of the discharge mapping are presented in Addendum 2 to the TZW FSP (Integral 2006b).

C3.8.3.2.1 Stratigraphic Coring Results

A total of five stratigraphic cores were collected offshore of the Willbridge site to improve the understanding of the offshore hydrogeology (Figure C3.8-5). The stratigraphic cross section presented in Figures C3.8-3a–c was updated with the data collected from these cores, as were the cross sections presented in Integral (2006e).

All of the core logs show the presence of a thick silt unit extending from at or just below the mudline to a depth of 30–35 ft. This unit is consistent with the projection of the silt alluvium layer underlying the site into the river (Figures C3.8-3a–c) and with the predominance of silt indicated by the surface sediment texture (Figure C3.8-4). The silt unit was continuous at all of the core locations, with the exception of GW-D5, in which a 4-ft-thick layer of sand with silt was observed at a depth of 14 to 18 ft bml. This sand layer may be a buried feature related to the former Holbrook Slough. A petroleum odor and moderate sheen was observed in this section of the core, suggesting the buried feature may be a pathway for groundwater transport.

The surface sediments at locations GW-D3, GW-D4, and GW-D5 all consisted of silt. A 1-ft-thick surficial sand layer overlying a 3-ft-thick clay layer was present at the surface of core GW-D1, and a 1-ft-thick surficial sand and gravel layer was present at GW-D2. Slight to moderate petroleum odors and/or sheen were recorded in the surface sediments from cores GW-D2, GW-D3, and GW-D5. A basal layer of basalt gravel was encountered at 32 ft bml in GW-D3, and a plug of basalt was observed at the bottom of core GW-D5 (29.5 ft bml).

C3.8.3.2.2 Surface Sediment Texture

Figure C3.8-4 presents the interpreted distribution of offshore sediment textures based on the Trident observations, grab samples, and past sediment sampling events. The vast majority of the surface sediments were silt. At the upstream end of the site, a nearshore zone of sandy sediments was observed. This zone then transitioned to a significant zone of mixed sand and silt. A small, isolated zone of sand and silt was also observed at the downstream end of the site—extending approximately 50 to 150 ft from the shoreline.

C3.8.3.2.3 Trident Probe Temperature Mapping

The Trident probe temperature mapping locations and results are shown on Figure C3.8-4. The groundwater discharge mapping effort spanned the entire shoreline, extending both upstream and downstream of the site boundaries. The Trident data indicate several general patterns. Nearshore silts showed generally minimal temperature signals. There were a few exceptions to this trend—most notably locations W4-C and W1-A. The two locations in the upstream sand zone showed strong temperature signals, as did several of the locations in the upstream mixed sand/silt zone. Location W2-B, in the downstream mixed sand/silt zone, displayed significant temperature signals as well.

C3.8.3.2.4 Seepage Flux Measurement

Seepage meters capable of recording time-series positive and negative flux were installed at seven of the Trident locations offshore of the Willbridge Site: W2-B, W4-C, W7-C,

W9-A, W9-C, W10-C, and W12-A (Figure C3.8-4). These locations were selected to quantify groundwater discharge rates in areas where the Trident profiling indicates potential discharge, paying particular attention to the southeastern half of the site, including the area of the former Holbrook Slough. The locations are designated WSEEP 2B, WSEEP 4C, WSEEP 7C, WSEEP 9A, WSEEP 9C, WSEEP 10C, and WSEEP 12A (Figure C3.8-4).

Positive seepage meter flow averages were recorded at all but one location: WSEEP10C. This is the farthest offshore location evaluated and is situated on the outer edge of the upstream mixed sand/silt zone. A high seepage rate (average 13.6 cm/day) was recorded in the nearshore sand zone at location WSEEP 12A. Significant positive discharge was also observed at locations WSEEP 4C (average 3.9 cm/day), WSEEP 7C (average 2.7 cm/day), WSEEP 9A (average 7.1 cm/day), and WSEEP 9C (average 2.8 cm/day). These results suggest that groundwater is discharging to nearshore sediments adjacent to the Willbridge site, particularly in the area offshore of the Chevron and ConocoPhillips terminals. Although positive, the seepage rate recorded at location WSEEP 2B (average 0.4 cm/day) was low relative to other locations evaluated offshore of the site, suggesting that this zone is a relatively minor groundwater discharge area.

C3.8.3.3 Interpretation of Groundwater Discharge Zones

Based on review of the combined lines of evidence of the groundwater discharge mapping (including review of site stratigraphy, upland groundwater contours and concentrations, sediment texture, Trident temperature results, and seepage meter results) and the TZW and sediment analytical chemistry data, approximate zones of groundwater discharge offshore of the Willbridge site were identified. These zones, and the locations of TZW and sediment samples, are indicated on Figure C3.8-6.

The combined lines of evidence suggest that the shallow groundwater and associated COI discharge are likely occurring primarily in the nearshore area adjacent to the site and may be more significant in the southeastern half of the site. Groundwater flow patterns, upland COI distributions, and the groundwater discharge mapping and seepage meter results all suggest that groundwater discharge is occurring in this area. Further, this finding is consistent with a potential influence of the buried former Holbrook Slough on groundwater flow. The high seepage rate recorded at location WSEEP 12A in the nearshore sand located at the upstream end of the site suggests this is an area of significant groundwater discharge. However, this area is somewhat removed from the primary zone of groundwater COIs.

C3.8.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

Based on the discharge mapping results, TZW samples were collected from seven locations offshore of the Willbridge site. Figure C3.8-6 shows the TZW sampling locations, and Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the Willbridge site.

At each location, a sample was collected within the top 30 cm of the sediments.²¹ The rationale for the sampling locations was as follows:

- Samples were collected from four locations (W-06-A, W-07-C, W-09-A, and W-09-C) in the nearshore area adjacent to the southeastern half of the site, where groundwater COI discharge is thought to be greatest.
- A sample was collected from the upstream nearshore sand zone at location W12-A, where a very strong seepage rate was recorded. A second sample was collected from the sand zone at R2-W-02 in an area closer to the zone of known upland groundwater COIs associated with the site.
- One sample was collected from the nearshore area adjacent to the northwestern half of the site at W-04-C, where a relatively high positive seepage rate was recorded.

C3.8.4.1 Major Ion Chemistry

Figure C3.8-7 presents a Piper diagram for the Willbridge site that shows major ion signatures for TZW and upland groundwater at the site, and compares them to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are linearly scaled from 0 to 2,200 mg/L. In addition, Table C3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the Willbridge site TZW and upland groundwater samples was typically -15 percent or less, with all of the samples being anion deficient, likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis. However, the charge balance for one TZW sample and three upland groundwater samples was greater than -20 percent, indicating considerable imbalance in the major ion fingerprint. As such, the major ion composition for these samples carries some uncertainty.

The major ion composition of the Willbridge TZW samples from the groundwater discharge zones is generally consistent with the composition of the upland groundwater chemistry. Both the groundwater and TZW major ion compositions are largely distinct from the major ion composition of the Willamette River water—particularly in the anion signature, which shows a greater influence of bicarbonate than is seen in the river water. These results suggest that the TZW major ion chemistry in the groundwater discharge zones is influenced by the discharging groundwater composition. However, because major ion data are not available for TZW in the low-to-no groundwater discharge zone, it cannot be determined if TZW in areas where groundwater is not discharging has the same major ion signature. This has been the case at the majority of the GWPA sites,

²¹ As described in Addendum 2 of the FSP (Integral 2006b), the original sampling plan called for collection of a second, deeper sample (target depth of 90 to 150 cm), if possible, at three locations (W-06-A, W-07-C, and W-09-A). These samples could not be collected because of the presence of fine-grained sediments at these locations and depths, which precluded sample collection using the Trident probe.

suggesting that the same general geochemical processes (e.g., mineral precipitation/dissolution) operate to determine the TZW and groundwater major ion composition.

C3.8.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figures C3.8-8a–c present the range in concentration of total BTEX, total PAHs, and total chromium observed in TZW and sediment samples collected from the two interpreted groundwater discharge zones and in sediment from the low-to-no groundwater discharge zone at the Willbridge site. These data are also presented in Table C3.8-1. No TZW samples were collected from the low-to-no groundwater discharge zone.

- **Total BTEX (Figure C3.8-8a)** – BTEX was detected at low concentration (<1 ppb) in one of three TZW samples from the higher rate groundwater discharge zone and in one of four TZW samples from the lower rate groundwater discharge zone. The detected BTEX concentrations were considerably lower than the concentrations present in upland groundwater. BTEX was below detection in the majority of the sediment samples collected offshore of the site, but was detected at low concentration in one sample each in the low-to-no and the higher rate groundwater discharge zones.
- **Total PAHs (Figure C3.8-8b)** – Total PAHs were detected at low concentration in two samples each from the higher rate groundwater discharge zone and the lower rate groundwater discharge zone. The detected concentrations in TZW were within the wide range of total PAH concentrations in upland groundwater. Sediment total PAH concentrations were largely consistent across the two groundwater discharge zones and the low-to-no groundwater discharge zone.
- **Total Chromium (Figure C3.8-8c)** – Total chromium was detected in the majority of the TZW samples collected from the two groundwater discharge zones, with slightly higher concentrations detected in the lower rate discharge zone. However, the TZW concentrations in this zone were low (<30 ppb) relative to upland groundwater chromium concentrations at the Willbridge site. The two groundwater discharge zones and the low-to-no groundwater discharge zone all exhibited a consistent range of sediment chromium concentration.

C3.8.5 Groundwater Pathway Assessment for the Willbridge Site

Based on an integrated analysis of all discharge mapping and sampling results, a nearshore area of higher-rate groundwater discharge was identified in the area of the former Hollbrook Slough. A lower-rate groundwater discharge area was also identified along the steep sediment face across the remaining area of the site shoreline. Outside of these areas, there is low-to-no groundwater discharge. These areas are indicated on Figure C3.8-6.

While the designations of groundwater discharge are well-supported, TZW samples generally do not show concentrations at the level observed in upland groundwater. Concentrations of petroleum-related chemicals in TZW concentrations are substantially lower than upland groundwater concentrations. Total chromium was detected in TZW,

but at generally low concentrations. Arsenic was present in TZW, consistent with the observations study-wide at the GWPA sites. The occurrence of arsenic in TZW is evaluated in detail in Section C4.0. Concentrations of total chromium measured in sediment samples from groundwater discharge zones offshore of the Willbridge site do not show elevated levels relative to sediment samples collected from low-to-no groundwater discharge zones. No TZW samples were collected in the low-to-no groundwater discharge zone for comparison with the groundwater discharge zones. TZW concentrations are not inconsistent with concentrations in upland groundwater; however, there remains some acknowledged uncertainty regarding the source of total chromium detected in TZW samples offshore of the Willbridge site.

C3.9 GUNDERSON AREA 1

The Gunderson site is an industrial facility located between RM 8.5 to 9.2 on the west bank of the Willamette River (Figure C1.3-1). The property is bounded by the river on the northeast, by NW Front Avenue to the southwest, Lakeside Industries to the northwest, and James River Corporation to the southeast (Figure C3.9-1). The BNSF's Lake Yard is located to the southwest across NW Front Avenue. The site itself is relatively flat, with buildings, asphalt pavement, railroad spurs, and parking lots covering approximately 85 percent of the property. The balance of the site consists of open ground and gravel-covered roadways. The riverbank is predominantly armored with riprap, although there are a few areas of vegetated shoreline where there is little or no riprap present. The Round 2 GWPA activities at the Gunderson site were focused on the northwest end of the site in an area termed "Area 1" in past site environmental investigations.

Gunderson, Inc. is an active industrial facility that manufactures and refurbishes railroad cars and marine barges. Historical operations by previous site operators (see Integral and GSI 2004) have also included ship dismantling, automobile salvage, landing craft manufacturing, and engineered steel component and specialty marine parts manufacturing. Painting, degreasing, sandblasting, automobile crushing and shredding, and hazardous material storage have been conducted at the site as part of current and historical operations.

A detailed discussion of Gunderson Area 1, including discussion of historical releases, source areas, and remedial measures is presented in the CSM site summary for the Gunderson site (Integral 2007a, 2007c).

The chemical concentration data referenced in this subsection for select COIs in upland groundwater samples, TZW samples, and collocated sediment samples associated with the Gunderson site are presented in Table C3.9-1.

C3.9.1 Nature and Extent of Groundwater Contamination

Historical site operations have resulted in impacts to site soil and groundwater. A primary source of contamination at the site was a spill in 1980 at the Gunderson facility

in Area 1 when the bottom of a process dip tank ruptured, releasing approximately 200 gallons of 1,1,1-trichloroethane (TCA; Integral and GSI 2004). In addition, releases of bunker C fuel, toluene, and other chemicals have been documented or are suspected at the site (Integral and GSI 2004).

Groundwater COIs associated with Area 1 of the Gunderson site include VOCs and metals. The primary VOCs include TCA and its degradation products and dichloroethene (DCE). Recent observed upland groundwater concentrations are presented in a series of figures in Appendix A-9 (Integral et al. 2005) and Addendum 2 to the TZW FSP (Integral 2006b). Figures C3.9-2a–c present the distribution of TCA, DCE, and total lead in groundwater at the site and in offshore TZW samples. For the reasons discussed above in Section C3.0.4, the depiction of upland groundwater conditions on these figures is based on the most recent available upland groundwater sampling data collected prior to the 2005 implementation of the GWPA. Figures C3.9-3a–b present the concentration of TCA and DCE on a representative stratigraphic cross section for Gunderson Area 1.

NAPL has not been encountered during any of the investigations of the Gunderson property (Squier|Kleinfelder 2005).

C3.9.2 Completed and Ongoing Remedial Measures

Three remedial systems are currently operating at the site, and a fourth is planned to go online in the near future. Figure C3.9-1 shows the approximate locations of these systems, which include the following:

- Groundwater has been extracted from well WEX-60 in Area 1 since November 2004 for the treatment of dissolved halogenated compounds associated with the 1980 TCA release (Squier|Kleinfelder 2005; King 2005, pers. comm.).
- A vapor extraction system installed in MW-31 is currently remediating the release of aromatic solvents (toluene) associated with the former 3,000-gallon UST and other historic surface impacts (Integral and GSI 2004; King 2005, pers. comm.).
- An air-sparge/soil-vapor-extraction system (AS/VES) for the pipeline containment is located on the Gunderson property to remediate identified gasoline-related impacts to vadose-zone soils and groundwater (Integral 2005a). This remediation system was installed by Texaco in 1998 and is currently operated by Equilon. The remediation system includes six soil vapor extraction wells and four air-sparge wells (SMW-1 through SMW-10; King 2005, pers. comm.; Integral 2005a).
- Supplemental groundwater TCA remediation using an AS/VES was implemented in 2005.

Following a 1998 pipeline rupture, phase-separated, hydrocarbon-impacted soil was excavated from the vicinity of the Gunderson parking lot and removed from the site (Integral 2005a; King 2005, pers. comm.). Soil was excavated over an area of 12 ft by 18 ft and to a depth of 8 ft.

Outside of Area 1, additional groundwater source control evaluations are ongoing in Gunderson Areas 2 and 3, according to the September 2010 DEQ Milestone Report (DEQ 2010).

C3.9.3 Evaluation of Groundwater Discharge

Groundwater discharge mapping was performed at the Gunderson site during the summer 2005 GWPA field effort to help focus the subsequent TZW sampling. This investigation was performed in accordance with the Round 2 Groundwater Discharge Mapping FSP (Integral 2005c). Detailed results of the discharge mapping are presented in Addendum 2 of the TZW FSP (Integral 2006b).

In addition, based on data gaps identified after the completion of the Round 2 GWPA investigation, a Round 3 GWPA field investigation was completed between October 16 and October 19, 2007. During this investigation, stratigraphic cores were collected offshore of the Gunderson Area 1 site for the Round 3 GWPA, in accordance with the Round 3 GWPA FSP (Integral 2007c). The objectives of the Round 3 GWPA field program were designed to address a data gap identified by USEPA in its June 8, 2007 letter (USEPA 2007, pers. comm.) to the LWG regarding Round 3 data needs to complete the RI/FS. From discussions with USEPA and Oregon DEQ at a meeting on June 27, 2007, the LWG understands these data need to focus on concerns about whether there is a possible in-river discharge of a chlorinated solvent plume offshore of the Gunderson Area 1 site. The specific portion of the plume of interest is a possible remnant plume in the deep conductive (sand/gravel) zone downgradient of the capture zone of Gunderson's source control well. USEPA's expressed concern was that this contamination may be discharging into the river in an area beyond the limits of the Round 2 GWPA investigation at the site (Integral 2006f). Results of the Round 3 investigation are provided in Integral (2007c).

C3.9.3.1 Site Hydrogeology and Groundwater Flow Patterns

Figures C3.9-3a and b present a representative geologic cross section for the Gunderson site amended with groundwater and TZW quality data. In addition, Figures C3.9-4a–d present stratigraphic cross sections extending from the site across the river based on the stratigraphic coring completed during the Round 2 and Round 3 investigations (Section C3.9.3.2.1).

The general site stratigraphy consists of three geologic units: alluvium and younger terrace deposits, a gravel zone, and basalt bedrock. These units and their corresponding hydrogeologic unit characteristics are discussed below:

- **Alluvium and Younger Terrace Deposits** – The Gunderson facility is underlain by recent alluvial deposits of the Willamette River. The portion of the site adjacent to the Willamette River was raised above the river level using dredged material beginning in the 1930s. The alluvial deposits consist of discontinuous zones of transitional sands, sandy silt, silts, and some clay, interfingering across the site. The unit is typically 30 to 40 ft thick in Area 1, but is significantly

thicker in other site areas. This shallow unit has been subcategorized into a surficial sand and fill zone (containing concrete and other debris), a predominantly silt zone, and an underlying predominantly sand zone (Squier/Kleinfelder 2005).

- **Gravel Zone** – Gravels are present at the base of the recent alluvial deposits in some, but not all, of the borings. The gravel zone is primarily encountered as a north/south trending channelized feature in Area 1, where it overlies the basalt and may act as a preferential pathway. There is not an evident in-river discharge point for this potential preferential pathway.
- **Basalt Bedrock** – Flows of the CRBG are present directly beneath the shallow sediments and gravels. The CRBG slopes uniformly east into the Willamette River at about 0.03 ft/ft and then steepens to about 0.1 ft/ft as the CRBG plunges below the Willamette River. Basalt was encountered in Area 1 borings at approximately 50–60 ft bgs.

Preferential transport of chlorinated VOCs may be occurring in the deep gravel zone beneath Area 1. This gravel zone extends under the river below the bottom of the channel.

As a remedial measure, the Gunderson site has been operating an extraction well downgradient of the 1,1,1-TCA spill location since November 2004 (Section C3.9.2). The Area 1 groundwater gradient is relatively flat as a result of ongoing pumping from the remediation extraction system. It is possible that VOC contamination downgradient of the extraction well and outside of the hydraulic capture zone is present as a “remnant plume” within the more conductive materials (sand and gravel) above the bedrock. The hydraulic gradient in the area indicates that this remnant plume will flow to the north; however, the Round 3 stratigraphic coring suggests there is not a complete pathway for such a remnant plume to the river.

C3.9.3.2 Groundwater Discharge Mapping Field Investigation

In 2005, discharge mapping was performed at the Gunderson site, in accordance with the Discharge Mapping FSP (Integral 2005c), to help focus the subsequent TZW sampling effort. In all, 28 in-river measurements were made with the Trident probe. The Trident probe collected temperature and conductivity data above and below the sediment surface, as well as sediment texture information. Ultrasonic seepage meters were installed for 24-hr periods at six of the Trident locations offshore of the site. Two offshore stratigraphic cores (plus one replicate core) were collected to improve the understanding of the offshore stratigraphy. Core logs were used to update the stratigraphic cross sections. Screening samples of TZW were collected with the Trident probe at 10 locations at a depth of 60 cm below the sediment surface interface. The 2007 Round 3 GWPA included stratigraphic coring at nine locations offshore of the Gunderson Area 1 site to fill data gaps identified during the Round 2 investigation.

C3.9.3.2.1 Stratigraphic Coring Results

Two stratigraphic cores (E1 and E2) were collected offshore of the Gunderson site during the Round 2 GWPA to improve the understanding of the offshore stratigraphy. In addition, nine stratigraphic cores were installed during the Round 3 GWPA investigation. The locations of the stratigraphic cores are shown in Figure C3.9-4a.

The stratigraphic information from the offshore coring program, coupled with existing upland stratigraphic information, indicates a widespread, uniform, and thick upper fine-silt layer (12–20+ ft thick, with the exception of core C05, which has a very silty sand lens at a depth of 9 ft bml) extending well out into the center of the channel. The gravel layer was encountered at the bottom of the three cores collected closest to the west shoreline (C01, C02, and C07). A sweet, acrid smell was noted by the field geologist in the gravel zone in cores C01 and C02. No odor was noted at any other interval in any other core. The gravel was not encountered in the remaining cores, which were all completed to the planned depth of 40 ft. This suggests that if the gravel zone continues, it increases in depth bml offshore of the Gunderson site. A thick, lower sand zone, below the upper silt, was encountered in all but one (C03) of the remaining cores farther offshore.

The flame ionization detector (FID) readings were taken across all of the Round 3 cores, except where recovery was 0 percent. With the exception of readings at cores C02, C03, and C04, the FID readings were generally comparable to slightly higher than (by a factor of 2 or 3)²² FID readings from Round 2A cores collected in the area but outside of any projected path of the TCA plume. These readings (excluding C02, C03, and C04) likely reflect the depositional zone and the known presence of methane in subsurface sediments in the area (per the 2001 sediment profile imaging survey).

C3.9.3.2.2 Surface Sediment Texture

Figure C3.9-5 presents the texture of surface sediments offshore of the site based on data obtained from the Round 2 investigation, Round 3 investigation, and historical surface sediment sample descriptions. Based on this surface texture mapping, the entire Study Area offshore and downstream of Area 1 consists of predominantly silty surficial material. Gravel on top of the silt was observed just offshore of the Lakeside Industries dock at locations GN3-D and GN4-C. Limited areas characterized by silty sand or sand occur at the upstream end of the Equilon dock and in the nearshore area between the upstream Gunderson dock and the shoreline.

C3.9.3.2.3 Trident Probe Temperature Mapping

The Trident probe temperature mapping locations and results are shown on Figure C3.9-5. Although the Gunderson Trident data indicate generally higher temperature

²² The factor of 2 to 3 increase in FID readings, relative to Round 2A measurements, is attributed to the performance of these measurements immediately after sample collection during this event. In contrast, during Round 2A, core samples were transported to the field lab and exposed to a warm and dry atmosphere during logging before FID samples were collected and measured. This is expected to result in significant loss of volatile materials, lowering the FID reading.

differences in the upstream transects (GN5, GN6, and GN7), temperature differences across the site are generally low relative to those observed at other sites. The only location with a temperature difference greater than 4°C was GN5-A. Notably low temperature differences (<1°C) were observed just offshore of the Lakeside Industries dock, where gravel was observed on top of the silt layer (likely introduced to stabilize bottom sediments at this high traffic location). Seepage meters were placed at locations where Trident measurements could not be taken (GN1-E and GN4-E) to verify that no discharge is occurring at these areas. Seepage meters were also deployed at locations in the path of the TCA plume, where temperature and or conductivity differences indicated possible discharge or where verification of no discharge was desired.

C3.9.3.2.4 Seepage Flux Measurement

Seepage meters capable of recording time-series positive and negative flux were installed at six locations offshore of the Gunderson site: GN1-E, GN2-E, GN3-B, GN4-A, GN4-C, and GN4-E. These seepage meter locations are designated GNSEEP1E, GNSEEP2E, GNSEEP3B, GNSEEP4A, GNSEEP4C, and GNSEEP4E. Average results of the seepage meter measurements are presented in Figure C3.9-5.

The highest maximum discharge rate was observed at nearshore seepage meter location GNSEEP4A, with a maximum rate of 3.4 cm/day and an average rate of 1.3 cm/day. The three seepage meters deployed farthest offshore (GNSEEP1E, GNSEEP2E, and GNSEEP4E) measured seepage rates that varied slightly between positive and negative flux, averaging near zero. The location in the gravel just offshore of the Lakeside Industries dock, GNSEEP4C, indicated a small net negative discharge as did location GNSEEP3B. These results indicated that groundwater discharge through the thick silt layer is minimal. The only significant discharge in the path of the TCA plume is likely occurring in the nearshore area around GN4-A and possibly GN5-A, which had an even stronger temperature signal than GN4-A.

C3.9.3.2.5 Screening Sample Results

Screening samples of transition zone water were collected with the Trident at 10 locations at a depth of 60 cm below the sediment water interface. Because all locations were primarily silty, sampling was attempted at silty locations contrary to the original plan to focus only on sandy areas. Notes were kept on achievable purge rates and sampling rates for consideration in conjunction with the analytical results. Samples were analyzed for the full project suite of VOCs. Results for chlorinated VOCs, including TCA, dichloroethane (DCA), TCE, DCE, and vinyl chloride are presented on Figure C3.9-5. Locations where sampling flow rates were less than 5 mL/min are noted. At these locations, volatiles may have been lost during the sampling process due to slow filling of the sample containers. All locations without this designation had sampling flow rates greater than or equal to 60 mL/min.

Screening sample results agree with Trident temperature mapping and seepage meter results. The only measurable concentrations of VOCs were observed at the nearshore locations GN4-A and GN5-A, which are in the projected path of the TCA plume. Two

other locations, GN3-C and GN7-A, had adequate sample flow rates, but still showed no detected VOCs in the screening samples. The other six locations with undetected VOC results had very low sampling flow rates. While these low flow rates may have resulted in loss of volatiles during sampling, they are also indicative of the poorly conductive material in the zone being sampled.

C3.9.3.3 Interpretation of Groundwater Discharge Zones

All available lines of evidence, including the upland gradient, the sediment texture result, stratigraphic coring and FID measurements, the Trident and seepage meter results, and the screening sample results, indicate that there is minimal groundwater discharge offshore of Area 1 at the Gunderson site. The area of interest identified by the discharge mapping work is the nearshore area in the projected path of the TCA plume around locations GN4-A and GN5-A. This is supported by seepage meter results and screening sample results. Additionally, the Round 3 GWPA coring investigation indicates that there is not a remnant plume (which migrated before operation of the remediation system) along the path of the TCA plume farther offshore. This finding is consistent with the offshore seepage meter results, which demonstrated minimal groundwater discharge.

Based on review of the combined lines of evidence of the groundwater discharge mapping, approximate zones of groundwater discharge offshore of the Gunderson site were identified. These zones are indicated on Figure C3.9-6, along with the TZW and sediment sampling locations. One small, nearshore area is designated as a groundwater discharge zone. This designation is based primarily on seepage meter results of low positive average discharge (1.3 cm/day) and the spatial patterns of upland groundwater COIs in the TZW sampling results. The remaining offshore zone is designated as a low-to-no groundwater discharge area based on five seepage meter measurements, the stratigraphic understanding of the site, and the lack of chlorinated VOC detections in the five TZW sampling locations in this area (vinyl chloride was detected in a single sample at a concentration of less than 0.1 µg/L).

C3.9.4 Evaluation of Groundwater, TZW, and Sediment Chemistry

Based on the discharge mapping results, 10 transition zone water samples were collected from seven locations. Figure C3.9-6 shows the TZW sampling locations, and Table C3.0-1 summarizes the sample counts, sampling methods, and analyte groups represented in the TZW data set collected offshore of the Gunderson site. At each location, a sample was collected within the top 30 cm of the sediments. A second sample was collected from depths ranging from 90 to 150 cm at three of the locations. The rationale for the sampling locations was as follows:

- Samples were collected from four locations in and around the nearshore area where positive discharge was measured and chlorinated VOCs were present in screening samples (GN-03-A, GN-04-A, GN-04-B, and GN-05-A). A second, deeper sample was collected at GN-04-A (90 cm) and GN-05-A (150 cm).

- Three samples were collected farther offshore in the path of the TCA plume, where small positive discharges were observed and screening samples were not collected. These locations (R2-GN-1, GN-01-E, and GN-02-E) were positioned to evaluate the potential for residual groundwater-related COIs from migration of the plume before installation of the remediation system. A paired sample was collected from a depth of 150 cm at GN-01-E.

C3.9.4.1 Major Ion Chemistry

Figure C3.9-7 presents a Piper diagram for the Gunderson site that shows major ion signatures for TZW and upland groundwater at the site and compares it to that of surface water samples collected from the river at the Morrison and St. Johns bridges. Included in this figure is a table summarizing the data presented in the Piper diagram. The symbols in the central, diamond-shaped plot are linearly scaled from 0 to 2,200 mg/L. In addition, Table 3.0-3 presents the major ion concentration data and charge balance associated with this plot. The charge balance achieved for the Gunderson site TZW and upland groundwater samples was typically -15 percent or less, with the majority of the samples being anion deficient likely due to carbon dioxide offgassing from the sample prior to the laboratory analysis. However, the charge balance for one TZW sample and several upland groundwater samples was greater than -20 percent, indicating considerable imbalance in the major ion fingerprint. As such, these data carry considerable uncertainty.

The major ion composition of the Gunderson TZW samples from the interpreted groundwater discharge zone is similar to that of samples from the low-to-no groundwater discharge zone. However, the TZW samples from the low-to-no groundwater discharge zone group tightly together, while several of the TZW samples from the groundwater discharge zone show slightly differing cation and anion fingerprints. The TZW major ion compositions are largely distinct from the major ion composition of the Willamette River water. Most of the upland groundwater samples have a similar, albeit slightly differing, major ion composition to the TZW samples. The groundwater samples tend to show greater sodium and chloride influences than the TZW samples, which, on the contrary, show greater calcium and carbonate influences. Four of the upland groundwater samples show significantly higher chloride influences, and generally greater TDS levels, than TZW, river water, or other Gunderson groundwater samples.

Collectively, the major ion composition data suggest that, while TZW major ion composition may be slightly influenced by the discharging groundwater composition, influences from interactions (e.g., mineral precipitation/dissolution, microbial processes, etc.) within the sediment pore water environment are also significant.

C3.9.4.2 Distribution of COIs Relative to Groundwater Discharge Zones

Figures C3.9-8a–d present the range in concentration of DCE, TCE, total chromium, and lead observed in TZW and sediment samples collected from the interpreted groundwater discharge zone and the low-to-no groundwater discharge zone at the Gunderson site. These data are also presented in Table C3.9-1.

- **DCE and TCE (Figures C3.9-8a and b)** – DCE and TCE were detected at low concentration in TZW from the nearshore groundwater discharge zone at the site. No TZW data are available for the low-to-no groundwater discharge zone. DCE and TCE were not detected in sediments.
- **Total Chromium (Figure C3.9-8c)** – Chromium was detected at low concentration in TZW from the groundwater discharge zone and in two of five samples from the low-to-no groundwater discharge zone. TZW total chromium concentrations were generally lower than those measured in upland groundwater. Chromium was detected at similar concentrations in sediments from the low-to-no groundwater discharge zone and the groundwater discharge zone.
- **Lead (Figure C3.9-8d)** – Lead was detected at low concentration in the groundwater discharge zone and was comparable to the lower end of the range of concentrations observed in upland groundwater. Lead was below detection in the TZW samples from the low-to-no groundwater discharge zone. Sediment lead concentrations were not substantially different across these two zones.

C3.9.5 Groundwater Pathway Assessment for the Gunderson Site

Based on an integrated analysis of all discharge mapping and sampling results, a nearshore area of groundwater discharge was identified at the Gunderson site. This discharge area is indicated on Figure C3.9-6. Discharge (flow) rates are likely to be low in this zone due to suppression of the groundwater gradient by upgradient extraction wells; this interpretation is supported by the seepage meter result from this area, which recorded a 24-hr average discharge of 1.3 cm/day. Low level concentrations of COIs were detected in TZW from this groundwater discharge zone. These COIs are likely the result of migration of upland groundwater COIs prior to installation of the remediation system extraction wells. The data suggest that ongoing migration of the chemicals to the TZW via groundwater discharge does not contribute to significant concentrations of COIs in nearshore TZW sediments.

The stratigraphic information collected in the Round 2 and Round 3 coring efforts creates a clear and consistent picture of offshore stratigraphy across the three transects: a thick silt layer extends out into the center of the channel; the more conductive sand and gravel layers are located beneath this silt; and the gravel layer was only observed nearshore, indicating that if it continues offshore the layer increases in depth with distance offshore (>40 ft bml). Collectively, the stratigraphic information does not indicate a conductive pathway for any remnant TCA plume.

C4.0 GEOCHEMICAL ANALYSIS OF ARSENIC, BARIUM, AND MANGANESE IN TZW

Arsenic, barium, and manganese were detected in many of the TZW samples collected from offshore of all nine of the sites evaluated during the GWPA (see Section C3.0). The ubiquity of these metals/metalloids in TZW raises questions regarding whether their occurrence is a function of natural conditions (i.e., background), the direct or indirect result of chemical releases to upland groundwater, or the result of *in situ* biogeochemical processes occurring within sediments. Chemical releases to upland groundwater may be direct sources of these metals (e.g., historical use of arsenical pesticides), or they may cause releases of these metals indirectly, by altering the subsurface biogeochemical conditions, resulting in metals releases by mineral dissolution or desorption reactions within the subsurface soil/aquifer matrix. For example, the degradation of petroleum-related compounds in upland groundwater plumes may produce conditions conducive to the desorption and/or dissolution of metals in the subsurface. Similarly, the oxidation of natural and/or contamination-related organic carbon present in sediments may influence oxidation-reduction (redox) conditions in a manner that would influence the solubility and mobility of arsenic, barium, and manganese in TZW.

This section presents an analysis of the occurrence of arsenic, barium, and manganese in TZW offshore of all nine of the study sites. TZW concentrations of these metals are compared to the concentrations observed in nearshore upland groundwater at each of the nine sites and in Study Area wells identified by DEQ as representative of area-wide “background” (i.e., wells that are located upgradient of known or suspected groundwater impacts).

In addition, an evaluation is provided of the geochemical conditions likely governing the solubility of these metals/metalloids in TZW. The objective of this analysis is to identify the geochemical controls that may be affecting the origin, transport, and fate of the metals/metalloids in the subsurface environment and assess if the occurrence of these metals in TZW is controlled solely by the geochemistry of the associated sediment or is also influenced by upland groundwater plume transport to the groundwater-sediment transition zone. A primary focus of this analysis will be the intersection between redox geochemistry and the solubility of iron and manganese species in aqueous systems. Under oxidizing conditions in subsurface aqueous systems, iron oxide minerals (and to a lesser extent manganese oxides) commonly exist as coatings on soil, aquifer, or sediment particles and provide an adsorbent phase for many otherwise soluble metals, including arsenic and barium (as well as other metals and metalloids). Under geochemically reducing conditions, iron and manganese may be used as a terminal electronic acceptor by biological processes. This results in the dissolution of oxide minerals, with the concurrent release of iron, manganese, and sorbed metals such as arsenic and barium. As discussed further below, the equilibrium solubility of barium- and arsenic-bearing mineral phases that may exist in the TZW-sediment environment are also extensively considered in this analysis.

The following presents an evaluation of the occurrence of arsenic, barium, and manganese in TZW and, where data are available, nearshore upland groundwater at each of the nine GWPA sites. This evaluation is intended to determine if there are notable differences across the sites or if a similar range of concentration occurs at each of the sites, which would suggest that similar processes regulate the concentrations of these metals in TZW.

Several sources of data were compiled and evaluated to support this analysis. For TZW collected from the nine GWPA sites during the RI, Table C4.0-1 summarizes the concentrations of dissolved arsenic, barium, and manganese in filtered Trident and small-volume peeper samples.²³ The available arsenic, barium, and manganese concentration data in upland groundwater for the nine TZW study sites, which were obtained from the upland parties during the RI, are summarized in Table C4.0-2.

There are no data available on background concentrations of arsenic, barium, and manganese in TZW from a designated reference area for the Portland Harbor Site. A literature review was conducted in an effort to evaluate if the observed levels of arsenic, barium, and manganese in Study Area TZW are consistent with the concentrations of these metals observed in similar TZW environments elsewhere in the world. However, data of this nature are not widely published. Only limited data are available and, in many cases, the available data are from impacted sediments in estuarine or marine environments. Table C4.0-3 summarizes the results of the literature review. These data, though limited, suggest that the range of arsenic, barium, and manganese concentrations observed in Study Area TZW (Table C4.0-1) are generally comparable to the concentrations observed at other locations around the world. This finding is consistent with the hypothesis that concentrations of arsenic, barium, and manganese in the TZW are controlled by common biogeochemical processes (e.g., oxidation of natural organic carbon or the biological degradation of petroleum contamination) occurring in sediment environments, rather than by influences from upland groundwater plume discharges.

A systematic evaluation of background metals concentrations in upland groundwater in the vicinity of the Study Area has not been undertaken. However, at the request of USEPA, DEQ compiled a summary of upland sites with background monitoring wells that would support an analysis of Study Area background conditions (USEPA 2009, pers. comm.). Table C4.0-4 summarizes the available data for arsenic, barium, manganese, and iron (included to support the geochemical analysis; Section C4.3) in the Study Area background wells identified by DEQ.

Additionally, arsenic, barium, and manganese are known to occur naturally in groundwater from the shallow alluvial aquifers of the Willamette basin. A study by the USGS reports the following concentrations in the groundwater from these aquifers (Hinkle 1997).

²³ The statistical analysis was limited to filtered Trident and small-volume peeper samples as these best represent the dissolved fraction of arsenic, barium, and manganese in TZW.

Metal	Range in Concentration (µg/L)	Median Concentration (µg/L)
Arsenic	<1 to 2	2
Barium	4 to 30	8
Manganese	<1 to 58	2

Because these data are based on sampling of only 10 groundwater wells, they may not be representative of the groundwater conditions in the Study Area. These concentrations are on the low end of the concentrations observed in TZW and upland groundwater at the nine GWPA sites. This observation is also consistent with the hypothesis that metals in the TZW originate from common biogeochemical processes occurring in sediment environments, rather than from upland groundwater discharge.

Section C4.1 below gives an overview of the distribution of arsenic, barium, and manganese at the Study Area scale, and it presents results of statistical tests that were performed to determine whether concentrations of arsenic, barium, and manganese in TZW differed significantly among the nine study sites. Section C4.2 presents a site-by-site analysis of statistical and spatial relationships among arsenic, barium, and manganese concentrations in the groundwater discharge zones offshore of each site, in nearshore upland groundwater, and in background groundwater. An analysis of geochemical factors that may be influencing or controlling the solubility, mobility, and concentration of these metals within the shallow TZW environment is the focus of Section C4.3. Finally, Section C4.4 provides the overall conclusions supported by this analysis.

C4.1 STUDY AREA EVALUATION OF ARSENIC, BARIUM, AND MANGANESE CONCENTRATIONS IN TZW AND UPLAND GROUNDWATER

Some variability in TZW metals/metalloid concentrations is expected based on the nature of the sample collection technique and the location-specific variations in geochemistry. The majority of the TZW samples were collected using the Trident sampler at a depth of 30 cm; however, several samples were also collected using the small-volume peepers, which produce an integrated sample over the top 38 cm of sediment. In general terms, dissolved metal concentrations are expected to be lower in the oxic sediments near the sediment-water interface (top few centimeters of the sediment column) due to adsorption of metals to oxides and higher in the deeper, anoxic sediments where active biological reductive dissolution of oxides occurs. As a result, differences in concentrations between samples will depend on the relative depths of these two zones and the method of sample collection. In addition, the samples were collected at different periods of the tidal cycle, and tidal pumping may cause concentrations to vary widely as a function of time.

Concentrations of dissolved arsenic, barium, and manganese in background groundwater, upland groundwater at the nine study sites, and TZW at the nine study sites are compared in Figures C4.1-1 to C4.1-3. On each figure, background groundwater concentrations are shown in the far left column, followed by the site-specific groundwater and TZW data ordered by river mile. At many of the sites, the concentration ranges of arsenic, barium,

and manganese in TZW were generally similar (i.e., median concentrations at each site vary within about one order of magnitude), although the concentration ranges at some of the sites departed from the typical patterns. For example, median concentrations of dissolved arsenic in TZW are lower at Gasco and Willbridge than elsewhere, whereas dissolved barium concentrations appear to be higher than elsewhere at Arkema. Median dissolved manganese concentrations in TZW do not vary more than an order of magnitude among all nine sites.

The range in arsenic concentrations in the Study Area background wells is below the ranges in nearshore groundwater for the nine GWPA sites (Figure C4.1-1), while the arsenic concentration range in TZW across the nine sites broadly brackets the background groundwater range. Only total (unfiltered) concentrations of barium and manganese were reported for the background wells; no data are available for dissolved concentrations. Total concentrations of barium (Figure C4.1-2) and manganese (Figure C4.1-3) in background groundwater are generally slightly lower than the range of concentration of these metals measured in Study Area TZW and in upland groundwater.

Statistical testing was performed as described below to determine whether concentrations of arsenic, barium, and manganese in TZW differed significantly among the nine study sites. The distributions of arsenic, barium, and manganese in the TZW data sets were tested for normality using the Shapiro-Wilk test and/or for lognormality using the Kolmogorov-Smirnov test. No data sets passed tests for normality at the 0.05 level of significance. Distribution testing and visual inspection of the arsenic data indicated the TZW arsenic results do not fit a lognormal distribution (Figure C4.1-4). Distribution testing and visual inspection of the log-transformed TZW data for both barium and manganese suggest that the results for these metals both approach a lognormal distribution (Figures C4.1-5a and b and C4.1-6a and b). Analysis of Variance (ANOVA) testing of the barium data set based on a lognormal distribution resulted in a p-value of 0.00199—indicating that differences in barium concentrations among the sites are statistically significant. ANOVA testing for the manganese data set resulted in a p-value of 0.0587, which suggests that differences in manganese concentrations among all sites approaches, but does not reach, statistical significance at a level of 0.05 ($p \leq 0.05$).

In addition, non-parametric statistical analysis using the Kruskal-Wallis Test was performed to evaluate whether the arsenic, barium, and manganese concentrations in filtered shallow (≤ 38 cm bml) Trident and small-volume peeper TZW samples from any one site differed from those at the other sites at a significance level of 0.05 ($p \leq 0.05$).²⁴ Results are provided in Table C4.1-1. For manganese, no statistically significant differences were identified in TZW from any one site compared with the rest of the sites. Non-parametric statistical testing did, however, identify statistically significant differences with respect to arsenic ($p=0.0218$) and barium ($p=0.0047$). Exclusion of the Arkema Chlorate Plant from the analysis eliminated the statistical significance for arsenic ($p=0.3019$), indicating that the concentrations of arsenic in TZW at the Chlorate Plant are

²⁴ The Gasco site data set also includes the samples collected from 15.24 to 82.3 cm bml during the NW Natural's 2007 offshore investigation (Anchor 2008).

significantly different from (lower than) those at the other eight sites. Differences in barium concentrations remained significant ($p=0.0214$) even with the Arkema Chlorate Plant excluded, suggesting that the ranges in barium concentrations are more variable site-to-site than the other two metals.

Collectively, the statistical evidence suggests that the geochemical controls on manganese and arsenic are not generally influenced by site-specific conditions, such as the discharge of upland groundwater. The exception is arsenic concentrations in TZW adjacent to Arkema, which are lower than offshore of the other eight sites (Figure C4.1-1). For barium, statistical tests indicate possible differences between sites.

C4.2 SITE-SPECIFIC EVALUATION OF ARSENIC, BARIUM, AND MANGANESE IN TZW AND UPLAND GROUNDWATER

This section presents a site-by-site discussion of the occurrence of arsenic, barium, and manganese in TZW and groundwater. The particular emphasis of this discussion is to determine, at an individual site level, whether spatial and/or statistical relationships can be discerned between metals concentrations in the various groundwater discharge zones offshore of each site and upland groundwater.

In the subsections below, for each of the nine GWPA study sites, the TZW sampling results for arsenic, barium, and manganese are plotted discretely by groundwater discharge zone, along with the available site-specific upland groundwater and background groundwater results for these metals. The purpose of these plots is to evaluate if there are discernable spatial patterns in TZW metals concentrations in groundwater discharge zones versus areas where little-to-no groundwater discharge was observed. These plots are shown in Figures C4.2-1 to C4.2-27 and are discussed further below for each of the nine GWPA sites.

Additionally, concentrations of arsenic, barium, and manganese in TZW (filtered Trident and small-volume peeper samples), nearshore upland groundwater, and Study Area background groundwater were compared statistically, using the non-parametric Mann-Whitney U-test, to available data for these metals in nearshore upland groundwater and in the Study Area background wells as identified by DEQ (Table C4.2-1). Due to the varied spatial distribution, sampling depth, and collection methods represented in the compiled upland and background groundwater data sets, this statistical comparison of groundwater and TZW metal concentrations is considered a preliminary analysis that is used in support of other lines of evidence in the geochemical analysis. All TZW and groundwater values below laboratory detection limits were set to one-half the detection limit for the Mann-Whitney U-tests. The largest upland groundwater data set exists for arsenic, with upland groundwater data available for all sites except Gunderson (Figure C4.1-1). For barium, upland data were available for four sites: Kinder Morgan Linnton, ARCO, Siltronic, and Willbridge (Figure C4.1-2). Nearshore upland groundwater data for manganese are available for Siltronic and Arkema only (Figure C4.1-3). Results of these tests are summarized in Table C4.2-1 and discussed for each site in the individual subsections below.

C4.2.1 Kinder Morgan Linnton

Figures C4.2-1 to C4.2-3 present the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the Kinder Morgan Linnton site, and compare these concentrations to those measured in Study Area background groundwater wells. Arsenic concentrations observed in TZW samples from the groundwater discharge zone are comparable to the high end of the range of those measured in TZW from the low-to-no groundwater discharge zone (Figure C4.2-1). The arsenic concentrations in TZW from both of these zones are comparable to the concentrations observed in the nearshore upland groundwater and also span a similar concentration range as that of background groundwater (0.074 to 11.6 µg/L in TZW versus non-detect to 8.56 µg/L in background groundwater).

Barium and manganese concentrations observed in TZW samples from the groundwater discharge zone are comparable to the range of those measured in TZW from the low-to-no groundwater discharge zone (Figures C4.2-2 and C4.2-3). With the exception of a single barium result for TZW (125 µg/L), the concentrations of barium in TZW at the Kinder Morgan Linnton site are very similar to the concentrations in background groundwater (Figures C4.1-2 and C4.2-2). TZW manganese concentrations at the Kinder Morgan Linnton site fall at the upper end of the concentration range measured in background groundwater, but are consistent with the concentrations measured in TZW and upland groundwater at the other eight GWPA sites (Figure C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The differences in concentrations of arsenic and barium in TZW and nearshore upland groundwater from the Kinder Morgan Linnton site are not statistically significant ($p \geq 0.05$). No data are available for manganese in upland groundwater at the Kinder Morgan Linnton site.
- The analyses found statistically significant differences ($p \leq 0.05$) in the concentrations of arsenic and manganese in TZW from the Kinder Morgan Linnton site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area. However, differences in the barium concentrations in TZW and background groundwater were not statistically significant ($p = 0.297$).

C4.2.2 ARCO

Figures C4.2-4 to C4.2-6 illustrate the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the ARCO site, and compare these concentrations to those measured in Study Area background groundwater wells. Arsenic concentrations were similar in upland groundwater and in TZW from the groundwater discharge zone and the low-to-no groundwater discharge zone (Figure C4.2-4). The arsenic concentrations in TZW from both of these zones are comparable to the concentrations observed in the upland groundwater. TZW arsenic concentrations at the

ARCO site are slightly higher than the concentrations measured in background groundwater, but are comparable to the concentrations measured in TZW at the other eight GWPA sites (Figure C4.1-1).

Similarly, barium and manganese concentrations observed in TZW samples from the groundwater discharge zone are comparable to the range of those measured in TZW from the low-to-no groundwater discharge zone (Figures C4.2-5 and C4.2-6). TZW barium concentrations offshore of the ARCO site are consistently higher than the concentrations measured in background groundwater, whereas manganese concentrations in TZW fall within the upper range of background groundwater concentrations. Concentrations of both metals in TZW offshore of the ARCO site are consistent with the concentrations measured at the other eight GWPA sites (Figures C4.1-2 and C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The differences in concentrations of arsenic and barium in TZW and nearshore upland groundwater from the ARCO site are not statistically significant ($p \geq 0.05$). No data are available for manganese in upland groundwater.
- The analyses found statistically significant differences ($p \leq 0.05$) in the concentrations of arsenic, barium, and manganese in TZW from the ARCO site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area.

C4.2.3 ExxonMobil

Figures C4.2-7 to C4.2-9 illustrate the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the ExxonMobil site, and they compare these concentrations to those measured in Study Area background groundwater wells. Dissolved arsenic concentrations in TZW were comparable to the upper part of the range for nearshore upland groundwater in all three of the discharge zones mapped offshore of the ExxonMobil site (Figure C4.2-7). In general, the ranges of arsenic concentrations in TZW and nearshore upland groundwater are higher than the range of arsenic concentrations measured in background groundwater wells, but are consistent with the concentrations measured at the other eight GWPA sites (Figure C4.1-1).

Barium and manganese concentrations observed in TZW samples from the groundwater discharge zones are comparable to the range of those measured in TZW from the low-to-no groundwater discharge zone (Figures C4.2-8 and C4.2-9). The ranges of TZW barium and manganese concentrations at the ExxonMobil site are generally higher than the ranges of concentrations measured in background groundwater, but are consistent with the concentrations measured at the other eight GWPA sites (Figures C4.1-2 and C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The difference in arsenic concentrations in TZW and nearshore upland groundwater at the ExxonMobil site is not statistically significant ($p \leq 0.05$). No data are available for barium and manganese in upland groundwater.
- The analyses found statistically significant differences in the concentrations of arsenic, barium, and manganese in TZW from the ExxonMobil site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area.

C4.2.4 Gasco

Figures C4.2-10 to C4.2-12 present the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the Gasco site, and compare these concentrations to those measured in Study Area background groundwater wells. Arsenic concentrations were similar in TZW samples collected from the variable nearshore discharge zone and the low-to-no groundwater discharge zone, and they were also comparable to the range of concentrations measured in offshore groundwater samples (Figure C4.2-10). The ranges of arsenic concentrations in TZW and in offshore groundwater are higher than the ranges of arsenic concentrations measured in nearshore upland groundwater and background groundwater wells, but are generally consistent with, to slightly lower than, the TZW arsenic concentration ranges measured at the other eight GWPA sites (Figure C4.1-1).

Similarly, barium and manganese concentrations observed in TZW samples from the groundwater discharge zones offshore of the Gasco site are comparable to the range of those measured in TZW from the low-to-no groundwater discharge zone (Figures C4.2-11 and C4.2-12). The ranges of barium and manganese concentrations in TZW offshore of the Gasco site are consistently higher than the concentration ranges measured in background groundwater, but are consistent with the TZW concentrations measured at the other eight GWPA sites (Figures C4.1-2 and C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The difference in concentrations of arsenic in TZW and in nearshore upland groundwater at the Gasco site is statistically significant ($p=0.008$). No data are available for barium and manganese in upland groundwater.
- The analyses found statistically significant differences in the concentrations of arsenic, barium, and manganese in TZW from the Gasco site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area.

C4.2.5 Siltronic

Figures C4.2-13 to C4.2-15 present the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the Siltronic site, and compare these concentrations to those measured in Study Area background groundwater

wells. The available data suggest that the occurrences of arsenic in TZW from the nearshore, offshore, and low-to-no groundwater discharge zones are comparable to one another (Figure C4.2-13). No arsenic data are available for TZW from the far offshore groundwater discharge zone. TZW arsenic concentrations are somewhat lower than those in upland groundwater at Siltronic, and they slightly exceed the upper end of the arsenic concentration range in Study Area background wells (Figure C4.1-1).

Barium and manganese concentrations observed in TZW samples from the groundwater discharge zones offshore of the Siltronic site are comparable to the range of those measured in TZW from the low-to-no groundwater discharge zone (Figures C4.2-14 and 4.2-15). The concentration ranges of these metals in TZW are generally lower than those observed in nearshore groundwater. In contrast, the range in concentrations of these metals in TZW offshore of the Siltronic site is generally higher than the concentrations measured in background groundwater, but is consistent with the TZW concentrations measured at the other eight GWPA sites (Figures C4.1-2 and C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The difference in concentrations of arsenic in TZW and in nearshore upland groundwater at the Siltronic site is statistically significant ($p=0.013$), with the TZW samples exhibiting generally lower arsenic concentrations than upland groundwater. The differences in barium and manganese concentration between these two waters were not statistically significant ($p\geq 0.05$).
- The analyses found statistically significant differences in the concentrations of barium and manganese in TZW from the Siltronic site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area. The differences in arsenic concentration between Siltronic TZW and background groundwater, however, are not statistically significant ($p=0.444$).

C4.2.6 Rhone Poulenc

Figures C4.2-16 to C4.2-18 present the range of concentrations of arsenic, barium, and manganese observed in TZW and, where available, nearshore upland groundwater at the Rhone Poulenc site, and compare these concentrations to those measured in Study Area background groundwater wells. (No nearshore groundwater sampling results for barium and manganese are available for the Rhone Poulenc site.) Arsenic concentrations in TZW from the various groundwater discharge zones offshore of the Rhone Poulenc site fell well within the wide range of concentrations observed in nearshore upland groundwater (Figure C4.2-16). Although only a single sample was collected from the low-to-no groundwater discharge zone, the concentration of arsenic in the sample was comparable to the concentrations observed in other site TZW samples. The range of arsenic concentrations in TZW was consistently higher than the range observed in the background wells.

Barium and manganese concentrations observed in TZW samples from the groundwater discharge zones offshore of the Rhone Poulenc site are comparable to the concentration of these metals measured in the TZW sample from the low-to-no groundwater discharge zone (Figures C4.2-17 and C4.2-18). The concentration ranges of these metals in TZW are generally higher than the concentrations measured in background groundwater, but are consistent with the concentrations measured at the other eight GWPA sites (Figures C4.1-2 and C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The difference in concentrations of arsenic in TZW and in nearshore upland groundwater at the Rhone Poulenc site is not statistically significant ($p=0.101$). No data are available for barium and manganese in nearshore upland groundwater.
- The analyses found statistically significant differences in the concentrations of arsenic, barium, and manganese in TZW from the Rhone Poulenc site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area.

C4.2.7 Arkema

Figures C4.2-19 to C4.2-21 present the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the Arkema site, and compare these concentrations to those measured in Study Area background groundwater wells. Although limited to one data point, the reported arsenic concentration in TZW from the low-to-no groundwater discharge zone is within the range for the nearshore groundwater discharge zone but higher than the range for the variable groundwater discharge zone (Figure C4.2-19). Arsenic concentrations in TZW at Arkema are more variable than, but have a lower median value than, concentrations observed in nearshore upland groundwater and in background groundwater (Figure C4.1-1). The concentrations of arsenic in TZW offshore of the Arkema site are also generally lower than concentrations measured in TZW at the other eight GWPA sites (Figure C4.1-1).

Barium concentrations observed in TZW samples from the groundwater discharge zones offshore of the Arkema site are generally lower than in the low-to-no groundwater discharge zone, whereas this pattern is not as evident for manganese (Figures C4.2-20 and C4.2-21). Manganese concentrations in TZW fall within the range measured in nearshore upland groundwater at the Arkema site; nearshore groundwater sampling results for barium are not available. The concentration ranges of barium and manganese in TZW offshore of the Arkema site are consistently higher than the concentration ranges measured in background groundwater. The ranges of concentrations of barium in Arkema TZW are higher than the TZW concentrations measured at the other eight GWPA sites (Figure C4.1-2). Manganese concentrations in TZW from Arkema are also at the upper end of the range for the other sites (Figure C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The difference in concentrations of arsenic in TZW and in nearshore upland groundwater at the Arkema site is statistically significant ($p=0.00030$); however, the difference in manganese concentrations is not ($p=0.543$). No data are available for barium in nearshore upland groundwater.
- The analyses found statistically significant differences in the concentrations of barium and manganese in TZW from the Arkema site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area. The differences in arsenic concentration between Arkema TZW and background groundwater, however, are not statistically significant ($p=0.082$).

C4.2.8 Willbridge

Figures C4.2-22 to C4.2-24 present the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the Willbridge site, and compare these concentrations to those measured in Study Area background groundwater wells. Arsenic was detected in all seven of the TZW samples collected from the groundwater discharge zones (Figure C4.2-22). Several of the samples exhibited concentrations consistent with those measured in upland, nearshore groundwater, while two were at considerably lower concentrations. No TZW samples were collected from the low-to-no groundwater discharge zone offshore of the Willbridge site. Overall, the range of TZW arsenic concentrations offshore of the Willbridge site somewhat exceeded the range in background groundwater.

As with arsenic, no data are available for barium and manganese concentrations in TZW from the low-to-no groundwater discharge zone at the Willbridge site (Figures C4.2-23 and C4.2-24). Barium concentrations in TZW offshore of the Willbridge site fall within or below the lower end of the range measured in nearshore upland groundwater; nearshore groundwater sampling results for manganese are not available. The concentrations of barium and manganese in TZW offshore of the Willbridge site are comparable to or higher than in background groundwater, but they are generally slightly lower than the concentrations measured in TZW at the other eight GWPA sites (Figures C4.1-2 and C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- The difference in concentrations of barium in TZW and in nearshore upland groundwater at the Willbridge site is statistically significant ($p=0.012$); however, the difference in arsenic concentration is not ($p=0.078$). No data are available for manganese in nearshore upland groundwater.

- The analyses found statistically significant differences in the concentrations of arsenic and manganese in TZW from the Willbridge site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area. The differences in barium concentration between Willbridge TZW and background groundwater, however, are not statistically significant ($p=0.568$).

C4.2.9 Gunderson Area 1

Figures C4.2-25 to C4.2-27 present the range of concentrations of arsenic, barium, and manganese observed in TZW and nearshore upland groundwater at the Gunderson site, and compare them to the concentrations of these metals in Study Area background groundwater wells. No data are available for arsenic concentrations in nearshore groundwater at this site. The ranges of arsenic concentrations in TZW from the groundwater discharge zone and the low-to-no groundwater discharge zone offshore of the Gunderson site were comparable to, but slightly exceeded, the range of concentrations observed in Study Area background wells (Figure C4.2-25).

Barium and manganese concentrations observed in TZW samples from the groundwater discharge zone offshore of Gunderson Area 1 are less variable, but within the range of, the concentrations of these metals measured in TZW samples from the low-to-no groundwater discharge zone (Figures C4.2-26 and C4.2-27). Manganese concentrations in TZW are near the high end of the concentration range in background groundwater, while barium concentrations in TZW range somewhat higher than background. The concentrations of both metals in TZW are consistent with the concentrations measured at the other eight GWPA sites (Figures C4.1-2 and C4.1-3).

The statistical analyses described in Section C4.2 above and summarized in Table C4.2-1 suggest the following:

- No data are available for arsenic, barium, and manganese in nearshore upland groundwater at the Gunderson site.
- The analyses found statistically significant differences in the concentrations of arsenic and manganese in TZW from the Gunderson site and the concentrations of these metals measured in groundwater identified by DEQ as being representative of background conditions for the Study Area. The differences in barium concentration between Gunderson TZW and background groundwater, however, are not statistically significant ($p=0.199$).

C4.3 ANALYSIS OF GEOCHEMICAL CONTROLS ON ARSENIC, BARIUM, AND MANGANESE IN STUDY AREA TRANSITION ZONE WATER

The ubiquity of the arsenic, barium, and manganese in TZW across the nine GWPA sites—including areas mapped as groundwater discharge zones and also areas where little or no groundwater discharge is occurring—points to the possibility that the geochemistry of the sediment-TZW environment may be a more important control on the occurrence

and concentrations of these metals/metalloids in TZW than the flux of upland groundwater to the transition zone at the nine study sites. The following presents an evaluation of the potential role of geochemical controls on arsenic, barium, and manganese concentrations in Study Area TZW.

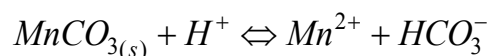
C4.3.1 Geochemical Controls on Metals/Metalloids in Aqueous Environments

Geochemical processes often mediate the aqueous concentrations of metals/metalloids in groundwater and sediments. The most important geochemical processes for many metals/metalloids are mineral precipitation/dissolution reactions and chemical adsorption to the surfaces of aquifer/sediment grains. Depending on the geochemical conditions, these processes can act either as a source or a sink of aqueous-phase inorganic constituents. The relative importance of these processes in a given aqueous system is strongly dependent on solution chemistry and aqueous speciation, pH, and redox state. The majority of the TZW samples are reduced (average oxidation-reduction potential [ORP] of -54 mV), calcium-carbonate waters of neutral pH. Table C4.0-1 presents a summary of the concentrations/levels of arsenic, barium, manganese, iron, pH, alkalinity, and ORP recorded in the TZW samples.

C4.3.1.1 Mineral Solubility

Inorganic chemicals can occur as ions, molecules, solid phases (minerals), adsorbed phases, or gases in the groundwater/TZW environment, with the relative distribution of chemical mass among these phases being a function of the system's thermodynamic energy and reaction kinetics. Thermodynamic constants, such as solubility products and equilibrium partition coefficients, describe the chemical energy of interaction between various chemical species and may be used to determine the relative distribution, or speciation, of the chemicals under thermodynamic equilibrium conditions. Ions in the groundwater/TZW environment will tend to distribute between aqueous, solid, and gas phases in a manner that minimizes the potential chemical energy (i.e., they tend to move toward thermodynamic equilibrium). However, some reactions are kinetically limited and occur very slowly and, as a result, may not exert a significant control on chemical concentrations in a transient environment (e.g., flowing groundwater/TZW).

Under thermodynamic equilibrium, a given mineral will tend to precipitate or dissolve depending on the presence or absence of the mineral in the sediment matrix and on the relative aqueous-phase concentrations of the individual ions that make up the mineral phase. As an example, the mineral rhodochrosite ($\text{MnCO}_{3(s)}$) precipitates (and dissolves) according to the following reaction:



The solubility of a mineral at equilibrium is defined by the mineral solubility product, or K_{sp} . For rhodochrosite, K_{sp} is defined by the concentrations of manganese (Mn^{2+}), bicarbonate (HCO_3^-), and the hydrogen ion (H^+):

$$K_{sp} = \frac{[Mn^{2+}] \times [HCO_3^-]}{[H^+]}$$

where the brackets denote activity (at low ionic strength, activity \approx molar concentration) of the given species under equilibrium conditions. Therefore, at equilibrium, the concentration of manganese in groundwater or TZW in contact with rhodochrosite is a function of the solution bicarbonate concentration and pH.

The conditions of any solution can be described using the ion activity product, Q_{sp} . The ion activity product is defined in the same manner as the solubility product, only it is based on the actual activities of the species present, which may or may not be at equilibrium. The tendency for a mineral to precipitate or dissolve under specific conditions in the environment is described by the saturation index (SI), which is defined as follows:

$$SI = \log \left(\frac{Q_{sp}}{K_{sp}} \right)$$

SI values of 0 indicate that the water is in equilibrium with the mineral phase. Non-zero SI values indicate that the water is not at equilibrium. Positive SI values indicate that supersaturated conditions are present and the tendency would be for the mineral to precipitate from solution. Negative SI values indicate undersaturated conditions and a tendency for the mineral (if present) to dissolve into solution. However, either under- or oversaturated conditions may be maintained for long periods of time due to kinetic limitations.

Activity diagrams are a useful tool for evaluating likely aqueous and solid-phase geochemical controls on the speciation of a given metal/metalloid. These diagrams demonstrate the stability fields of minerals and aqueous species over a range of conditions. The two primary variables affecting aqueous geochemistry are the redox state, measured as Eh (or ORP), and hydrogen ion activity, measured as pH. One of the most common forms of activity diagrams are Eh-pH diagrams, where stability fields of aqueous and solid phase species are mapped over a relevant range of Eh values and pH values. These diagrams are used to illustrate the Eh-pH conditions under which specific aqueous and mineral species are stable thermodynamically and likely to be influencing metal/metalloid chemistry and partitioning between dissolved and solid phases.

Evaluation of potential geochemical controls on metal/metalloid solubility based on the specific water chemistry measured in a given water sample is a complex, multi-variate problem. Computer models, such as Geochemist's Workbench (GWB) (Bethke 2006), are typically applied to assess geochemical conditions that are likely important for an observed water chemistry.

C4.3.1.2 Adsorption Processes

Adsorption processes often exert significant limitations on metal/metalloid mobility in aqueous subsurface environments. Common adsorbents in natural systems include iron, aluminum, and manganese hydrous oxides; amorphous silicates; and organic material (EPRI 1984). Iron and manganese oxides are often of particular importance, as they are frequently present in environmental systems as amorphous mineral coatings on soil and sediment grains and are characterized by high surface areas. Oxide minerals are amphoteric, meaning that their surface charges can vary from positive to negative as a function of solution pH. A result of this surface charge is that oxide mineral surfaces have the ability to complex with protons (H^+) and hydroxide (OH^-) ions from solution—favoring H^+ at lower pH and OH^- at higher pH. This results in the development of charged sorption sites capable of binding with ions, such as dissolved metals, due to electrostatic interactions. Cations (such as Ba^{2+} , Fe^{2+} , and Mn^{2+}) are more strongly adsorbed at higher pH values (where oxide surfaces tend to be negatively charged), while anions (such as AsO_4^{2-}) are more strongly adsorbed at lower pH values.

The affinity of metals/metalloids to adsorb to a given oxide surface and the influence of pH on adsorption efficiency vary by element and as a function of the water chemistry. Arsenic and barium are both known to adsorb to iron and manganese oxide minerals (Kabata-Pendias and Pendias 1992). Arsenic, which is typically present as an anion in environmental waters, is preferentially adsorbed under acidic to neutral pH conditions, whereas barium, which exists as a cation in environmental waters, is preferentially adsorbed under basic conditions (Stumm 1992).

Solution chemistry can significantly affect the tendency for a given metal to adsorb to mineral surfaces in the environment. For example, the formation of aqueous complexes can limit the availability of a given metal/metalloid for adsorption. Further, other ions may be present that can compete for the finite number of sorption sites on the mineral surface. A common example is competitive adsorption of phosphate (PO_4^{3-}) and arsenic. Phosphate and arsenic behave similarly in environmental systems, and it has been commonly observed that elevated phosphate effectively competes with arsenic for ion adsorption sites (e.g., Peryea and Kammereck 1997). This competition can result in decreased sorption and increased transport of arsenic through the environment.

C4.3.2 Geochemical Environment of the Sediment Transition Zone

Generally speaking, microorganisms gain energy through the process of respiration during which the microorganisms transfer electrons from organic carbon to a terminal electron acceptor (TEA). Oxygen is the most common and thermodynamically favorable of the TEAs, and aerobic respiration predominates in open systems (i.e., systems at equilibrium with the atmosphere). Because oxygen has limited solubility in water, it is often depleted in groundwater and TZW environments not in contact with the atmosphere. Frequently there is sufficient organic carbon present in these systems to support a reduced environment as microbial respiration shifts to alternate TEAs (i.e., anaerobic conditions). Common TEAs in groundwater systems, listed in order of energy

potential, include nitrate (NO_3^-), manganese (Mn^{4+}), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide (CO_2 ; methanogenesis).

Owing in part to its abundance in subsurface systems, ferric iron (Fe^{3+}) is one of the more important TEAs from a biogeochemical perspective (Chapelle 1993). Ferric iron (Fe^{3+}) is commonly present in saturated soil and sediment as hydrous oxide minerals. As microorganisms transfer electrons to Fe^{3+} , it is reduced to ferrous iron (Fe^{2+}), causing iron hydrous oxides to dissolve. As dissolution progresses, the surface area available for sorption decreases and the species sorbed to the mineral surface, including metals and metalloids such as barium and arsenic, are desorbed and can accumulate in the aqueous phase. Similar to Fe^{3+} , oxidized forms of manganese (e.g., $\text{MnO}_{2(s)}$) are common in subsurface systems and can serve as TEAs, resulting in the reduction of Mn^{4+} and a release of Mn^{2+} from the aquifer/sediment matrix to the groundwater/TZW solution.

In the event that Mn^{4+} and Fe^{3+} are depleted in a given groundwater/TZW system, sulfate-reducing conditions can be established. Under these conditions, sulfate (SO_4^{2-}), is reduced to sulfide (S^{2-}). When metal ions are present, sulfate-reducing conditions can result in the precipitation of highly insoluble metal-sulfide minerals.

Although manganese-reducing, iron-reducing, and sulfate-reducing conditions can be associated with sites where biodegradable organic chemicals (e.g., petroleum hydrocarbons) are present, reducing conditions frequently occur naturally due to influences of native organic carbon sources (e.g., natural organic matter in sediments and aquifer materials, infiltration of organic-rich water from a surface water body or wetlands). Sediments and the TZW environment in the Willamette River are influenced by both anthropogenic sources (e.g., overwater releases, influx of contaminated groundwater, stormwater discharge) and natural sources of organic matter (e.g., organic detritus). ORP measurements in TZW indicate that, in the areas investigated, the transition zone is frequently, though not ubiquitously, characterized by reducing conditions (Figure C4.3-1).²⁵ These ORP conditions and the frequent presence of dissolved iron in TZW samples suggest that sufficient organic carbon is present in many Study Area sediments to deplete oxygen and support manganese- and iron-reducing conditions. Sulfate-reducing conditions also likely occur in some locations; however, sulfate-reducing conditions typically occur at ORPs of <-300 mV (Vogel et al. 1987), and the TZW ORP data suggest that only a small number of TZW samples approach such conditions.

Sediment profile imaging (SPI) data collected throughout the river sediments are also consistent with a reduced sediment environment. Figure C4.3-2 presents, as an example of the typical sediment profile in the Study Area, an SPI image collected in silty sediments at SPI location 31A just offshore of the ARCO site, near TZW sampling

²⁵ As shown on Figure C4.3-1, ORP measurements in TZW offshore of the Siltronic site depart markedly from the ranges reported at the other eight sites. This difference may reflect differences in sampling methodologies; many of the TZW samples in the Siltronic data set were collected using a different sampling method (Geoprobe) than those used in the GWPA TZW sampling.

location R2-AR-2. The image shows the uppermost ~15 cm of the sediment profile. Two zones are visible—a lighter, brownish colored zone in the near-surface sediments and darker, grayish sediments at depth. The visible transition is referred to as the apparent Redox Potential Depth (RPD); in this image it occurs at approximately 3.2 cm. The near-surface sediments are lighter colored due the presence of iron hydrous oxide mineral coatings on the sediment particles, which is consistent with a mechanism in which iron precipitates from solution as the reduced TZW interacts with oxygenated river water. The darker zone at depth is below the apparent RPD and indicates a reduced TZW environment. The apparent RPD has been mapped for sediments throughout the Portland Harbor Study Area (SEA 2002). The RPD is typically ~3 cm below the sediment surface, but can range from less than a centimeter to more than 20 cm. The open areas below the RPD on Figure C4.3-2 are methane voids and indicate methanogenic conditions. Methanogenic conditions have been observed on a widespread basis in SPI images of shallow sediments in Portland Harbor, particularly in nearshore depositional areas (SEA 2002).

Redox conditions will vary with depth within the sediment column. Near-surface sediments are influenced by contact with the water column and associated dissolved oxygen. Deeper in the sediment column, less exchange with surface water occurs and, if sufficient labile organic carbon is present (i.e., carbon that is readily metabolized), the redox environment shifts to alternate TEAs and more reduced conditions. The SPI RPD data indicate that, on the whole, reduced conditions tend to be established over a relatively shallow depth (several centimeters) in the sediment column, although oxidized conditions extend to greater depths at some locations in the sediment bed. This understanding is consistent with the predominance of reduced conditions in the TZW samples, as the majority of the TZW water samples were collected using the Trident probe at a depth of 30 cm bml.

Figure C4.3-3 presents the TZW ORP versus the concentrations of total PAHs, TPH, and total organic carbon (TOC) measured in collocated sediment samples collected during Round 2. Figure C4.3-4 presents the TZW ORP data versus concentrations of total PAHs and TPH measured in TZW. Although these figures do not show a good correlation between ORP and these measures of organic matter abundance in TZW and sediment, they do suggest that even low levels of TOC in sediment can correspond with reduced TZW conditions and that these conditions are often present even in the absence of anthropogenic organic carbon sources (e.g., TPH, total PAHs). The poor correlation between ORP and TOC is not surprising, as TOC is a measurement of the bulk organic carbon content and not all of the organic carbon in the sediments is labile (i.e., readily metabolized by microorganisms).

Microbial activity can also significantly influence the geochemical environment of TZW and groundwater through the production of alkalinity. A primary end product of respiration is carbon dioxide (CO₂). In closed systems (i.e., water not directly in contact with the atmosphere), these processes can lead to an oversaturation of CO₂ and, in turn, the formation of carbonate/bicarbonate alkalinity. This process provides pH-buffering

capacity to the water (helping to maintain circum-neutral pH conditions) and can drive the formation of carbonate minerals.

C4.3.3 Geochemical Speciation Modeling of Arsenic, Barium, Iron, and Manganese in Transition Zone Water

Geochemical modeling analyses were performed to provide a better understanding of controls on the fate and transport of arsenic, barium, and manganese in the TZW. Because it is anticipated that arsenic and, potentially, barium concentrations will be strongly influenced by iron oxide solubility, geochemical controls on iron were also evaluated.

The geochemical modeling was conducted at two different levels. First, Eh-pH activity diagrams were created for each metal. These diagrams identify the aqueous or mineral species that should control metal mobility. Second, more detailed calculations were performed to predict speciation within the aqueous phase and to calculate the saturation index for minerals controlling metal solubility. These calculations were performed using the geochemical modeling software Geochemist's Workbench (GWB; Bethke 2006).

Selection of appropriate modeling parameters is important to ensure applicable results. Whenever possible, the modeling relied on measured data from TZW samples. This data set consisted of metal concentrations (arsenic, barium, iron, and manganese), major cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}), major anions (Cl^- , SO_4^{2-}), alkalinity, pH, and ORP. In addition, it was assumed that the system was not in contact with, and hence not in equilibrium with, the atmosphere. This assumption, which is based on the general isolation of sediment pore waters from the atmosphere, affects two primary variables—ORP and pH. Under this assumption, ORP will not be controlled by atmospheric oxygen, and the pH will not be controlled by equilibrium with atmospheric carbon dioxide.

All of the geochemical modeling assumed a temperature of 10°C and no equilibrium with atmospheric gases. Since the analysis was focused on the speciation of dissolved species, and the relation of this speciation to thermodynamic conditions, no solid mineral phases were assumed to be present. During the first two modeling efforts, the chemical data set was input into the “Spec8” module of GWB. The model output included speciation information (e.g., equilibrium activities of all aqueous species, including the three carbonate species [H_2CO_3], [HCO_3^-], [CO_3^{2-}]) and mineral saturation indices. To create Eh-pH diagrams, aqueous species activities were taken from the “Spec8” results and entered into the “Act2” module of GWB. The species activities chosen for the activity diagrams were median values from the complete set of TZW samples.

C4.3.3.1 Iron

Iron is a common trace element in rocks, soils, and sediments with an average crustal abundance of 7.1×10^4 mg/kg (Faure 1991). It is frequently present as oxide minerals (e.g., hematite, magnetite, goethite, lepidocrocite, and ferrihydrite) in soils (Kabata-Pendias and Pendias 1992). Iron is a redox-sensitive element, with the +2 and +3 oxidation states being the most important in the environment (EPRI 1984). Table C4.3-1

summarizes typical iron and iron oxide contents in suspended and bed sediments in rivers throughout the world, and includes studies specific to the Willamette River and Portland Harbor. These data indicate that iron is commonly present in suspended and river bed sediments, with typical total iron concentrations of about 4 percent. These concentrations are generally consistent with the average iron concentration (4.1×10^4 mg/kg or 4.1 percent) measured in near-surface sediments during the RI. In a study of suspended sediment in 33 rivers throughout the world, Poulton and Raiswell (2000, 2002) and Poulton and Canfield (2005) found that 40 to 51 percent of the iron in suspended sediments was present as iron oxide minerals, including hematite, magnetite, goethite, lepidocrocite, and ferrihydrite. Similarly, Hall (Hall et al. 1996) reported that 47 percent of the iron in lake bed sediment was iron oxide minerals. These data suggest that the deposition of particulate from the water column is a common source of iron oxide minerals to the sediment bed and is likely occurring in the LWR.

Figure C4.3-5 presents an iron Eh-pH diagram, which illustrates the predominant aqueous and mineral phases likely to be present in the TZW samples over a range of Eh and pH conditions. Under the circum-neutral pH and reducing conditions that characterize the majority of the TZW samples, the most important mineral phase for iron is the iron-carbonate mineral siderite [FeCO_3]. This finding is supported by the results of detailed speciation modeling, in which mineral SIs are calculated based on the water chemistry recorded in each individual TZW sample. As summarized in Table C4.3-2 and Figure C4.3-6, the SI of siderite varies from -2.94 to 2.40 across the range of TZW samples, and averages -0.302. These indices suggest that the aqueous concentrations of iron in TZW in many of the TZW samples are maintained at near-equilibrium with siderite (or an iron-bearing carbonate mineral such as calcite) in the sediment

Iron oxides are expected to be stable in suspended sediments within the river water column due to the presence of dissolved oxygen. However, as these suspended particles settle and become buried over time, these minerals would tend to dissolve under the reduced conditions that typically develop within the transition zone. This is consistent with the general correlation between TZW iron concentrations and ORP (Figure C4.3-8). Calculated SI values for the TZW (Table C4.3-2) are consistent with this hypothesis and indicate that TZW is typically undersaturated with respect to ferric iron hydrous oxide (SI range: -8.39 to 1.11; SI median: -3.18). As a result, if iron oxides are present in the sediment matrix, they would tend to dissolve into solution under the geochemical conditions measured in TZW. As is discussed previously, metals/metalloids such as arsenic and barium tend to strongly adsorb to iron (and manganese) oxides. As a result, the deposition of particulate iron oxides from the water column and their subsequent reductive dissolution within the sediment transition zone represents a potential source of these metals to TZW.

Iron concentrations in TZW are not well correlated to total PAH or TPH concentrations in the TZW samples (Figures C4.3-9 and C4.3-10). This suggests that other factors are more influential controls on redox and the solubility of iron oxide minerals in TZW. Further, as is shown in Figure C4.3-11, TZW concentrations of iron are also poorly

correlated to the TOC concentration in collocated sediment samples collected during Round 2. This is not unexpected, as sediment TOC is not a good measure of the availability of labile carbon (i.e., carbon that is readily metabolized) and microbial activity in the sediments.

C4.3.3.2 Manganese

Manganese is a common trace element in the lithosphere, with an average crustal abundance of 1,400 ppm (Faure 1991). It is frequently present as oxide minerals (e.g., pyrolusite [MnO_2 (s)] in soils (Kabata-Pendias and Pendias 1992), although rhodochrosite [MnCO_3 (s)] may control manganese solubility in reduced, alkaline environments (EPRI 1984). Manganese is a redox-sensitive element, with the +2, +3, and +4 oxidation states being the most important in the environment (EPRI 1984). Basalts, such as the Columbia River Basalt underlying the study location, have an average manganese concentration of 1,750 ppm (Faure 1991).

Table C4.3-1 summarizes typical manganese and manganese oxide contents in suspended and bed sediments in rivers throughout the world, and includes studies specific to the Willamette River and Portland Harbor. These studies indicate that manganese is commonly present in suspended and river bed sediments, with typical total manganese concentrations of about 0.1 percent. These concentrations are generally consistent with the average manganese concentration (656 mg/kg or 0.066 percent) measured in near-surface sediments during the RI. The various studies report a wide range of manganese oxide contents; however, two of the studies did not use extraction techniques specific to manganese oxides. The two studies that used selective extraction techniques for manganese oxides reported manganese oxide contents of 4 and 9 percent of the total manganese content. These data suggest that manganese oxides are common in suspended particulate and that particulate deposition is a likely source of these minerals to the sediment transition zone in the LWR.

Figure C4.3-12 presents a manganese Eh-pH diagram, which illustrates the predominant aqueous and mineral phases likely to be present in the TZW samples over a range of Eh and pH conditions. Under the circum-neutral pH and reducing conditions that characterize the majority of the TZW samples, the most important mineral phase for manganese is the carbonate mineral rhodochrosite. Aqueous Mn^{2+} is the most stable form of manganese in a lesser number of the TZW samples. This finding is supported by the results of detailed speciation modeling, in which mineral SIs are calculated based on the water chemistry recorded in each individual TZW sample. As summarized in Table C4.3-2 and Figure C4.3-13, the SI for rhodochrosite in TZW varies consistently between approximately 2 and -1 (weakly oversaturated to very weakly undersaturated) across the range of TZW samples. These indices suggest that the aqueous concentrations of manganese in TZW from all nine of the sites are maintained at near-equilibrium with rhodochrosite (or a manganese-bearing carbonate mineral such as calcite) in the sediment.

Calculated SI values (Table C4.3-2) indicate that TZW is undersaturated with respect to manganese oxide minerals (SI range: -16.4 to -4.6; SI median: -7.0). As a result, if manganese oxides are present in the sediment matrix, they would tend to dissolve into solution under the geochemical conditions measured in TZW. This is consistent with the previous discussion of dissolution of manganese (and iron) oxides in TZW, resulting in the concomitant release of adsorbed metals such as arsenic and barium. As discussed previously, manganese concentrations in TZW are not well correlated to TPH or total PAH concentrations in the TZW samples (Figures C4.3-9 and C4.3-10). This suggests that other factors are more influential controls on redox and the solubility of manganese oxide minerals in TZW. TZW concentrations of manganese are also poorly correlated to the TOC concentration in collocated sediment samples collected during Round 2 (Figure C4.3-11). This is not unexpected, as sediment TOC is not a good measure of the availability of labile carbon (i.e., carbon that is readily metabolized) and microbial activity in the sediments. The importance of redox cycling to the concentrations of manganese and other metals in pore water is well recognized. Hamilton-Taylor (1996a, 1996b) demonstrated that the oxidation of organic matter resulted in the dissolution of manganese in paired field-laboratory studies. Bryan et al. (1997) surveyed five Scottish lakes and found that the redox-related dissolution of manganese was a primary control on concentrations in pore water. Taylor and Boulton (2007) addressed the importance of manganese dissolution on the concentrations of manganese and metals sorbed to manganese-oxide phases.

The available upland groundwater data set is insufficient to perform the same geochemical analyses for the upland groundwater data. However, the alkalinity and pH values observed in upland groundwater (Table C4.0-2) are consistent with rhodochrosite solubility controls. This finding, coupled with the similarity of manganese concentrations between TZW and upland groundwater, suggests that manganese is likely naturally occurring in aquifer materials and river sediments throughout the Study Area and is unrelated to current or historical activities at the sites. The only exception to this conclusion is offshore of the Arkema site, where manganese is elevated in TZW relative to upland groundwater concentrations.

C4.3.3.3 Arsenic

Groundwater in the Willamette River Valley is known to contain areas with high levels of naturally occurring arsenic (Hinkle and Polette 1999). Arsenic is a redox-sensitive species, existing in the +3 and +5 oxidation states under aqueous environmental conditions. Under oxidizing conditions, the As(V) species (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-}) predominate, while under reducing conditions the As(III) species (H_3AsO_3 , H_2AsO_3^- , HASO_3^{2-} , AsO_3^{3-}) predominate (EPRI 1984). Arsenic is generally relatively soluble, with few arsenic-bearing mineral phases exerting controls on aqueous arsenic concentrations under typical environmental conditions. Arsenic sulfide minerals,

such as orpiment (As_2S_3) and realgar (As_4S_4) can be important under reducing and acidic conditions (EPRI 1984).²⁶

Figure C4.3-14 presents a stability diagram for arsenic based on median water quality conditions recorded in the TZW samples. The stability diagram suggests that under typical TZW conditions, arsenic is likely to be present as aqueous $\text{As}(\text{OH})_3$. The only mineral phases that might control the arsenic solubility are the arseno-sulfides orpiment and realgar. However, these phases only precipitate under conditions that are more reducing than any recorded at all but one of the TZW locations investigated. Although arsenic minerals are generally soluble, adsorption reactions to sediment/aquifer mineral grain surfaces frequently limit dissolved arsenic concentrations (Kabata-Pendias and Pendias 1992). Arsenic is particularly strongly adsorbed to iron oxide minerals, with the $\text{As}(\text{V})$ species having a greater affinity for the oxide surface than the $\text{As}(\text{III})$ species. Because arsenic is frequently present as an anion under typical environmental conditions, its sorption to oxide surfaces is favored at $\text{pH} < 8$ (Stumm 1992).

This geochemical speciation analysis indicates that mineral solubility controls are unlikely to be exerting significant influence on arsenic in the sediment/TZW environment. There is some evidence, however, that adsorptive processes are important factors for dissolved arsenic concentrations in TZW. As described above, iron and manganese oxide minerals are commonly present in suspended and near-surface sediments. Arsenic is likely to be bound to oxide minerals associated with suspended particulate matter within the river water column, and the deposition and burial of these particulates to the river bottom represents a source of arsenic to the sediment transition zone. As these particulates are buried, iron and manganese oxide minerals will tend to dissolve under the reduced conditions that predominate at a shallow depth within the sediment transition zone. As a result, less oxide mineral surface is available to adsorb arsenic and arsenic concentrations in TZW increase.

As illustrated in Figure C4.3-15, arsenic concentrations show an apparent correlation to manganese and iron concentrations in the TZW samples. Further, the concentrations of arsenic (as well as manganese and iron) tend to be elevated under reduced TZW conditions (Figure C4.3-8). Collectively, these data suggest that dissolution of manganese and iron oxide minerals under reducing conditions is resulting in the release of adsorbed arsenic to groundwater/TZW. This is consistent with the observations of Farmer and Lovell (1986), where in a study of lake sediment pore water, dissolved arsenic was found to increase with the dissolution of iron and manganese-oxides. However, as discussed above, siderite and rhodochrosite are thermodynamically stable under the Eh-pH conditions observed in most TZW samples, suggesting upper limits to dissolved iron and manganese concentrations may be imposed by precipitation of these

²⁶ Past research has suggested that the solubility of arsenic in the environment is limited by the formation of a highly insoluble barium-arsenate species— $\text{Ba}_3(\text{AsO}_4)_2(\text{s})$ (Chukhlantsev 1956). However, this solubility product has been long suspected to be questionable (EPRI 1984). More recent research suggests the mineral phase may be much less stable (Essington 1988)—a suggestion that has been supported by a recent study of groundwater with naturally occurring arsenic (Planer-Friedrich et al. 2001).

mineral phases. As a result, a simple linear correlation between arsenic concentrations and the concentrations of manganese and iron is not expected. However, Figure C4.3-15 does show that elevated arsenic concentrations tend to be associated with elevated concentrations of iron and manganese. Further, some fraction, if not all, of the dissolved iron and manganese in the TZW will re-precipitate as hydrous oxide minerals upon migration to the oxidized zone of the near-surface sediments of the river (iron-staining is a common cause for the lighter color of the near-surface sediments, Figure C4.3-2). Therefore, it is likely that dissolved arsenic migrating in TZW toward the sediment-surface water interface will be re-adsorbed to precipitated iron and manganese hydrous oxides in the oxidized near-surface sediment horizon as the pore water discharges to the surface water column.

As discussed previously, microbial processes driven by naturally occurring and/or anthropogenic organic carbon in the sediment/TZW environment are likely responsible for the reduced conditions in the TZW. These conditions typically result in higher concentrations of dissolved arsenic, iron, and manganese than in an oxidized environment. Further, as illustrated in Figure C4.3-7, arsenic concentrations tend to correlate with TZW alkalinity. This likely reflects microbial activity in the TZW/sediment environment (alkalinity is a result of the production of carbonate from microbial oxidation of organic matter which is coupled to the reductive dissolution of iron and manganese oxide minerals; see Section C4.3.2), resulting in reducing conditions.

Concentrations of arsenic, iron, and manganese are not well correlated to TPH or total PAH concentration in the TZW samples (Figures C4.3-9 and C4.3-10), suggesting that factors other than anthropogenic contamination in the sediment-TZW environment (e.g., naturally occurring organic materials) are contributing to conditions in the TZW environment that favor the dissolution of iron and manganese oxides and the possible concomitant release of arsenic. As is shown in Figure C4.3-11, TZW concentrations of arsenic, iron, and manganese are also poorly correlated to the TOC concentration in collocated sediment samples collected during Round 2. This is not unexpected, as sediment TOC is not a good measure of the availability of labile carbon (i.e., carbon that is readily metabolized) and microbial activity in the sediments.

C4.3.3.4 Barium

Barium is an alkaline earth cation that exists only at the +2 valence state in aqueous environments (EPRI 1984). The typical concentration of barium in basalt is 315 ppm (Faure 1991). Barium typically exhibits limited mobility in the environment due to its strong tendency to form sulfate and carbonate minerals and to be adsorbed by clay minerals. Barite ($\text{BaSO}_{4(s)}$) and witherite ($\text{BaCO}_{3(s)}$) are the predominant naturally occurring mineral forms of barium (Deer et al. 1966), but it can also occur as a minor component in more common carbonate minerals such as calcite (Lindsay 2001). Barium also is strongly adsorbed by clays and oxide minerals—particularly manganese oxides (Charette and Sholkovitz 2006). Researchers have shown that barium has a significantly greater affinity to manganese oxides than iron oxides (Charette and Sholkovitz 2006),

although both can be important determinants to the fate of transport of barium in the environment.

Figure C4.3-16 presents the Eh-pH stability diagram for barium in TZW. The stability diagram suggests that under typical TZW conditions, barium is likely to be present as aqueous Ba^{2+} . The strong correlation between dissolved barium and alkalinity concentrations measured in the TZW samples (Figure C4.3-7), suggests barium in TZW may be controlled by the dissolution of barium-bearing carbonate minerals such as witherite (BaCO_3), alstonite [$\text{BaCa}(\text{CO}_3)_2$], or, more likely, a common sedimentary carbonate mineral (e.g., calcite) in which barium is present as an impurity in substitution for calcium. The TZW samples are generally predicted to be undersaturated with respect to witherite and alstonite (a calcium-barium carbonate); however, the TZW is in approximate equilibrium with calcite (Table C4.3-2, Figure C4.3-17). In upland groundwater, the recorded pH and alkalinity (Table C4.0-2) are also consistent with carbonate mineral solubility controls on barium. Barite (BaSO_4) is generally undersaturated in the large majority of the TZW samples—suggesting that the TZW environment is depleted in dissolved sulfate relative to dissolved barium, and that any trace of barite present in the sediments as a mineral phase would therefore tend to dissolve. Exceptions to this are offshore of the Arkema Chlorate Plant area and at one location each offshore the Arkema Acid Plant area and Rhone Poulenc site, where TZW samples are oversaturated with respect to barite (Figure C4.3-18).

There is some evidence that adsorptive processes also may play a role in regulating dissolved barium concentrations in TZW. As illustrated in Figure C4.3-19, barium concentrations show an apparent correlation to iron and manganese concentrations in the TZW samples. These data suggest that the dissolution of iron and manganese oxide minerals under reducing conditions in the sediment/TZW environment may result in the release of adsorbed barium to TZW. This observation is consistent with the findings of Charette and Sholkovitz (2006), who found that the primary cause of elevated pore water concentrations of barium was the dissolution of sediment phase manganese oxides, which results in the liberation of sorbed barium.

C4.3.4 Geochemical Reaction Path Modeling of Arsenic, Barium, and Manganese in Transition Zone Water

The analyses presented in Sections C4.3.1 to C4.3.3 suggest the following processes are the primary geochemical controls on the solubility of arsenic, barium, and manganese in TZW:

- Microbial oxidation of labile organic carbon results in a moderately reduced TZW environment throughout the majority of the Study Area. Coupled to organic matter oxidation, TEAs such as iron and manganese oxide minerals are reductively dissolved. The reductive dissolution of oxide minerals deposited to the sediment bed with settling particulates is an important source of the iron and manganese detected in TZW.

- Manganese concentrations in TZW from all nine of the sites are maintained at near-equilibrium with rhodochrosite in the sediment, indicating that rhodochrosite (or other manganese-bearing carbonate minerals) is the primary control on manganese solubility in TZW. Similarly, iron concentrations in several of the TZW samples are maintained at near-equilibrium with siderite in the sediment, indicating that siderite (or other iron-bearing carbonate minerals) is an important control on iron solubility in TZW.
- Iron and manganese oxides are strong sorbents of metals/metalloids in the environment. The dissolution of oxide minerals in the sediment bed under reducing conditions will reduce the sorption capacity of the sediments, resulting in the release of any sorbed metals/metalloids to TZW. The release of adsorbed arsenic from iron and manganese oxides is likely a primary control on arsenic concentrations in TZW. Release of sorbed barium may also be an important contributor to TZW barium concentrations.
- Barium concentrations appear to be correlated with alkalinity in TZW, suggesting that barium concentrations are controlled by the solubility of a carbonate mineral, such as witherite or barium-containing calcite. Barite is undersaturated in TZW and, thus, if present in the Study Area subsurface materials, may also be a possible source of barium to TZW.

Geochemical reaction-path modeling using the USGS model PHREEQC (USGS 2007) was performed to evaluate if the above controls alone, in the absence of contributions of metals/metalloids from upland groundwater discharge through the sediments, are sufficient to account for arsenic, barium, and manganese concentrations that are consistent with the observed range in Portland Harbor TZW. Specifically, the modeling was undertaken to address two primary questions:

1. Can modest amounts of common minerals (iron and manganese oxides [and associated adsorbed arsenic and barium], witherite, barite) present in particulates deposited to the sediment bed provide sufficient mass of arsenic, barium, and manganese to the sediment transition zone to account for the observed concentration ranges in Study Area TZW?
2. Does the model simulation of the key geochemical processes described above (microbial oxidation of labile organic carbon coupled to reductive dissolution of iron and manganese oxide minerals, release of metals adsorbed to the oxide mineral surfaces, and dissolution of barium mineral phases) reasonably reproduce the range of measured conditions in Study Area TZW?

C4.3.4.1 Model Construction

A total of seven model simulations were conducted, including the base case model simulation and six additional model scenarios designed to evaluate the sensitivity of the model predictions to key model parameters. The matrix of model scenarios is

summarized in Table C4.3-3. The base case model scenario was established based on the following model construct:

- A representative composition for the Willamette River was established based on the median major ion chemistry observed at the USGS gauge at the Morrison Bridge.
- Goethite (FeOOH)²⁷ and birnessite (MnO_2) were added at concentrations of 10.6 and 0.467 mM, respectively.²⁸ These minerals were placed in equilibrium with the representative surface water composition, and the sorption of arsenic, barium, and other metals to these mineral surfaces predicted.²⁹
- Witherite was added at a concentration of 0.5 μM , which corresponds to 0.05 percent of the total barium content measured in the Study Area sediments.
- Calcite was added at a concentration of 0.1 M.³⁰
- Labile organic carbon, represented generically as CH_2O , was then incrementally titrated into the solid/solution mixture described above, to simulate the microbial respiration process and the development of reduced conditions within the TZW as increasing quantities of organic carbon are oxidized. CH_2O was added at increments of 0.2 μM over a total of 100 model steps (i.e., a total of 20 μM [60 mg/L] of CH_2O or 24 mg/L TOC was added).
- Rhodochrosite and siderite were allowed to form as secondary mineral phases at each titration step if the predicted conditions indicated that these minerals became saturated (i.e., $\text{SI} > 0$).

In addition to the base case, six model scenarios were conducted to evaluate the sensitivity of the model predictions to select model parameters. Each of these model scenarios are summarized below

- **Model Scenario 1** – Goethite and birnessite were added at 5x and 0.2x the base case concentrations, respectively, to evaluate the influence of increased abundance of goethite relative to birnessite on the model predictions.

²⁷ Goethite was selected over more amorphous forms of iron oxide (e.g., ferrihydrite), as minerals associated with suspended sediment in the water column are expected to have undergone considerable weathering. Further, use of goethite is considered conservative with respect to the adsorption of metals/metalloids, as ferrihydrite is estimated to contain 10x greater sorption site density than goethite (Dixit and Hering 2003).

²⁸ These concentrations correspond to 10 percent of the typical iron and manganese oxide contents in sediments reported in literature (see Section C4.3.3.1), and are set at conservatively low concentrations to illustrate that a small amount of oxide mineral (and adsorbed arsenic) mass in settled particulate can account for the observed metals/metalloid concentrations in TZW.

²⁹ The PHREEQC database was appended to include sorption constants for MnO_2 available from Appelo and Postma (1999).

³⁰ Calcite is a common mineral in the environment. Calculated SI values (Table C4.3-2) indicate that TZW is in approximate equilibrium with calcite (SI range: -6.26 to 1.49; SI mean: -0.59)

- **Model Scenario 2** – Goethite and birnessite were added at 0.2x and 5x the base case concentrations, respectively, to evaluate the influence of increased abundance of birnessite relative to goethite on the model predictions.
- **Model Scenario 3** – Witherite was added at a concentration of 21.0 μM (approximately 2 percent of the total barium content in Study Area sediments) to evaluate the influence of greater abundance of barium carbonate minerals on the predicted TZW barium concentrations.
- **Model Scenario 4** – Barite was added a concentration of 0.5 μM and witherite was excluded from the model, to evaluate if barite could provide a potential source of barium to TZW.
- **Model Scenario 5** – The SI for rhodochrosite was set at 1.0. This was done to evaluate the hypothesis that pure rhodochrosite may not actually form in the TZW environment and it may be more likely a solid solution of manganese in calcite. Setting the rhodochrosite SI to 1.0 is approximately equivalent to a 10 mole percent solid solution of manganese in calcite assuming ideal mixing.
- **Model Scenario 6** – The SI for siderite was set at 1.0. This was done to evaluate the hypothesis that pure siderite may not actually form in the TZW environment and it may be more likely a solid solution of iron in calcite. Setting the siderite SI to 1.0 is approximately equivalent to a 10 mole percent solid solution of iron in calcite assuming ideal mixing.

The input files for each of the seven model scenarios are provided in Attachment 2.

C4.3.4.2 Model Results

The results of the model simulations are presented in Figures C4.3-20 to C4.3-26 and are summarized in Table C4.3-3. Figures C4.3-20 to C4.3-22 present the model predicted results for pH, pe, and alkalinity, respectively; and Figures C4.3-23 to C4.3-26 present the model-predicted results for manganese, iron, arsenic, and barium, respectively. The model output files are provided in electronic format in Attachment 2. Specific findings with respect to key model parameters from the modeling exercise are summarized below:

- **Manganese (Figure C4.3-23)** – The model predicts that manganese oxide minerals will be readily reduced as a result of microbial respiration and oxidation of labile organic carbon in the transition zone. The concentrations of Mn^{2+} in TZW increase as a function of TOC oxidized and eventually achieve a plateau as rhodochrosite or manganese-bearing carbonate minerals form as a secondary mineral phase. When modeled to be in equilibrium with rhodochrosite, the model predicts a maximum manganese concentration in TZW of 2.5 to 3.3 mg/L (Table C4.3-3). When the rhodochrosite SI is set at 1.0, simulating a 10 mole percent manganese-calcite solid solution, the maximum TZW manganese concentration is predicted to be 24 mg/L (Table C4.3-3). The predicted range of maximum manganese concentrations from modeling is consistent with the

concentrations observed in Study Area TZW (median 2.47 mg/L; maximum 33.5 mg/L).

In most of the model scenarios, the pH is predicted to decline slightly (from 8.7 to 6.9 s.u.) as more TOC is oxidized (Figure C4.3-20). However, in model scenario 2, which involved 5x (2.3 mM) the concentration of birnessite added in the base case, the pH is predicted to rapidly increase to ~pH 11 in the initial steps of the model as the birnessite is reduced (Figure C4.3-21). Once birnessite is depleted in the model, the pH is predicted to rapidly drop back to circum-neutral levels. This predicted pH dynamic is not expected to occur in the transition zone environment, as naturally-occurring buffers not accounted for in the model are likely to maintain the pH in the near neutral range.

- **Iron (Figure 4.3-24)** – Goethite reduction is predicted to follow the reduction of birnessite, with Fe^{2+} concentrations steadily rising as a function of TOC oxidized before reaching a plateau as siderite or iron-bearing carbonate mineral forms as a secondary mineral phase. When modeled to be in equilibrium with siderite, the model predicts a maximum iron concentration in TZW of 4.5 to 5.2 mg/L (Table C4.3-3). When the siderite SI is set at 1.0, simulating a 10 mole percent iron-calcite solid solution, the maximum TZW iron concentration is predicted to be 14 mg/L (Table C4.3-3). The predicted range of iron concentrations from modeling is consistent with, albeit slightly lower than, the concentrations observed in Study Area TZW (median 25.2 mg/L). Smaller degrees of iron solid solution in calcite than assumed in the model (i.e. <10 percent) could readily explain the higher TZW concentrations.
- **Arsenic (Figure 4.3-25)** – Arsenic concentrations are predicted to be closely correlated to goethite dissolution and are predicted to increase to a plateau once the majority of the goethite is reduced. The maximum predicted arsenic concentrations from each of the model simulations ranged from 5.3 to 106 $\mu\text{g/L}$ (Table C4.3-3), depending on the amount of goethite added to the model. This range is comparable to that measured in Study Area TZW (0.21 to 65.4 $\mu\text{g/L}$; median 10.0 $\mu\text{g/L}$).
- **Barium (Figure 4.3-26)** – The model predicts that both witherite and barite would dissolve under the predicted TZW conditions, with the resulting barium concentration in TZW dependent on the amount of these minerals (or alternatively, a barium-bearing carbonate mineral such as calcite) present. The model simulations demonstrate that dissolution of only a small fraction (0.05 to 2 percent) of the total barium in the Study Area sediments can result in a similar range of predicted barium concentrations (0.075 to 2.9 mg/L; Table C4.3-3) to that observed in Study Area TZW (0.005 to 2.12 mg/L; median 0.068 mg/L). The model predicts that barium is only modestly sorbed to iron and manganese oxides, suggesting that reductive dissolution of these oxides (and concomitant release of adsorbed barium) represents a minor source of barium to TZW when compared to barium mineral dissolution processes.

The geochemical modeling presented here is a simplified representation of the complex TZW environment and is not intended or expected to exactly replicate TZW quality. The TZW geochemical conditions are expected to vary somewhat spatially (both laterally and with depth) as a function of several factors, including, but not limited to: 1) differences in the presence of labile organic matter available for microbial degradation, 2) localized differences in sediment mineralogy and grain size, 3) temporal influences on microbial activity (e.g., temperature), and 4) sediment permeability and the degree of exchange with surface water. The geochemical modeling is not intended to capture the range of these TZW conditions; rather the modeling is intended to simulate common geochemical processes expected to predominate the Study Area TZW and demonstrate that these conditions can readily explain the observed range of concentrations of arsenic, barium, and manganese in Study Area TZW.

Settling particulate matter from the LWR water column is likely to contain common minerals such as iron and manganese oxides and carbonates. The geochemical modeling presented here demonstrates that even modest concentrations of these minerals can readily provide sufficient metal/metalloid mass to the transition zone sediment to account for the concentrations of arsenic, barium, and manganese observed in the Study Area TZW. The TZW water quality data, as well as other data/information such as the SPI data, confirm that reducing conditions predominate at relatively shallow depths within the sediment column. The modeling illustrates that these reduced conditions are the result of the oxidation of labile organic matter and that, under such conditions, further oxidation of organic matter is coupled to reductive dissolution of manganese and iron oxide minerals associated with the sediments. A side-effect of these processes is the release of metals/metalloids adsorbed to the oxide mineral surfaces to solution. The modeling results further show that when sediment contains modest amounts of these minerals, these reactions can readily achieve the range of observed arsenic, barium, and manganese concentrations in Study Area TZW.

C4.4 CONCLUSIONS

An evaluation of TZW, available nearshore uplands groundwater data, and data representative of Study Area background conditions for groundwater, was performed to evaluate the occurrence of arsenic, barium, and manganese in TZW and to assess the geochemical conditions likely affecting the origin, transport, and fate of these metals in the subsurface environment of the LWR.

Statistical and spatial analyses demonstrated that the concentrations of manganese were not significantly different in TZW across all nine of the sites. For arsenic, concentrations were only different at the Arkema site, and for barium, differences in concentrations in TZW across the nine sites were found to be statistically significant (although the median concentrations observed at each site were generally similar; Figure C4.1-3). The results for manganese and arsenic are generally consistent with natural biogeochemical processes acting on all river sediment rather than site-specific groundwater discharges. For barium, site-specific differences were important, although the source of these differences cannot be determined on the basis of the statistical tests alone.

Visual comparisons made on TZW concentrations at individual sites were also consistent with sediment rather than upland groundwater sources. For this analysis, concentrations in TZW from areas identified as groundwater discharge zones were compared to TZW from areas where little-to-no groundwater discharge is taking place. Concentrations were not substantially different between locations, although there were relatively few samples for comparison at several of the sites.

Collectively, the statistical and spatial evidence suggests that the biogeochemical controls on manganese and arsenic are influenced by conditions that are typical of sediment environments (e.g., the presence of organic matter leading to reducing conditions). For barium, statistical tests indicate possible differences between sites, whereas visual comparisons were inconclusive.

A geochemical analysis of the sediment-TZW environment offshore of the nine TZW study sites identified the most likely biogeochemical processes governing arsenic, barium, and manganese concentrations in Study Area TZW. Key findings of this analysis include the following:

- Concentrations of metals are generally higher in TZW samples with negative ORP (reducing conditions) than positive ORP (oxidizing conditions). Metals concentrations in TZW also appear to be positively correlated with alkalinity. These observations are consistent with increased levels of microbial activity typically associated with river sediment—microbial respiration creates reducing conditions that result in increased aqueous solubility of the metals.
- Arsenic concentrations in TZW are not controlled by equilibrium with any arsenic mineral phases that would control its aqueous solubility. However, the geochemical environment of both TZW and nearshore groundwater was found to be generally consistent with iron- and manganese-oxide reducing conditions—suggesting that elevated arsenic concentrations in these waters likely result from reductive dissolution of naturally occurring sedimentary iron and manganese hydrous oxides and the concomitant release of adsorbed arsenic present at background levels.
- TZW samples collected in the Study Area are typically moderately oversaturated with respect to the mineral witherite, suggesting that this mineral or a barium-bearing carbonate mineral (e.g., calcite) may be controlling barium solubility. Barite is moderately undersaturated in the chemically reducing conditions typical of the transition zone. Dissolution of these minerals from the sediment matrix, if present, is a potential source of barium to TZW. In addition, it is likely that barium concentrations in TZW are also locally influenced by the release of adsorbed barium from clays, in addition to iron and manganese oxide mineral surfaces following their reductive dissolution during microbial respiration. However, these processes may be minor relative to mineral dissolution processes.
- Manganese in TZW from all nine sites is likely derived from reductive dissolution of sedimentary manganese oxides, and appears to be maintained at approximate

equilibrium with rhodochrosite or other manganese-bearing carbonate mineral (e.g., calcite).

- Re-precipitation of hydrous manganese and iron oxides minerals above the redox potential depth in near-surface sediments is likely to be a removal mechanism for dissolved manganese, barium, arsenic, and iron as TZW migrates into the oxidized zone of near-surface sediments, thereby limiting the dissolved mass flux of these elements out of the sediment.

Overall, geochemical conditions in the TZW environment are influenced by the presence of organic carbon sources (either natural or introduced) and associated microbial oxidation of organic carbon sources in the near-bottom sediment environment. This results in predominantly reducing geochemical conditions in Study Area TZW samples and associated sediments. Natural organic matter is abundant in shallow sediments in the Study Area (see RI Map H4.2-2 in Appendix H), and geochemical model simulations illustrate that microbial oxidation of natural organic matter, coupled with the above described geochemical controls, can reasonably explain the observed concentration ranges of these metals in Study Area TZW. The reaction-path modeling demonstrates that deposition of modest amounts of common mineral phases associated with suspended particulate in the water column, coupled with the reduced redox environment of the transition zone, results in the presence of arsenic, barium, and manganese in TZW. Further, the modeling demonstrates that these naturally occurring biogeochemical processes alone, (i.e., in the absence of any mass contribution to the transition zone from groundwater discharge) can readily reproduce the range of arsenic, barium, and manganese concentrations observed in Study Area TZW. This finding is consistent with the similarity in the concentrations of these metals/metalloids in TZW samples across all nine of the GWPA sites irrespective of whether or not the samples were collected from demonstrated zones of active groundwater discharge.

Based on this analysis, the occurrence of arsenic, barium, and manganese in Study Area TZW predominantly reflects the local geochemical conditions of the sediment-TZW environment of the Study Area and is independent of influences from migration of upland groundwater plumes to the LWR.

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